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Reactions of Alpha-Halosilanes.

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REACTIONS OF α-HALOSILANES

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John P. Jones
June, 1971

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ABSTRACT

While both the electronic configurations of silicon and carbon and their relative positions in the periodic table immediately suggest a similarity in the chemistry of these two elements, it may be suggested that the differentiating properties of carbon and silicon warrant the greatest attention. The work presented herein involves the study of the anomalous and heretofore unexplained effect of the triorganosilyl moiety on adjacent electron deficient centers.

A critical review of the literature revealed that a systematic study of the effect that the trialkylsilyl group has on electron deficient centers had yet to be undertaken. The present work employs a kinetic approach to this problem. The electron deficient center is generated in the form of an intermediate carbonium ion in solvolysis reactions of α-bromosilanes. 2-Bromo-2-trimethylsilylpropane (I) was prepared along with the analogous carbon system, dimethyl-t-butylcarbinyl bromide (II). Compound II was chosen as a model of normal S_N1 reactivity in solvolysis reactions. All evidence thus far obtained indicates that the solvolysis mechanism of I also involves a transition state which has considerable carbonium ion character. This allows for a direct comparison with the analogous carbon system (II) which has been shown to proceed along a similar reaction path. The results of comparing the experimental data obtained for I and II allow significant conclusions to be made concerning the modes of stabilization of carbonium ions by adjacent alkyl

groups and by the α-silyl group. The stabilizing effect of the former is ascribed to hyperconjugative interactions which are largely absent in the latter.

The aluminum chloride catalyzed rearrangement reaction of α-chlorovinylsilanes was also investigated. There was no rearranged product isolated under any of the reaction conditions employed.

CHAPTER I

The first reported organosilicon compound was prepared in 1863 when Friedel and Crafts reacted tetrachlorosilane with diethylzinc to form tetraethylsilane. However, it was not until the turn of the century with the development of the Grignard reagent and its use in preparing organosilicon compounds that organosilicon chemistry came into its own. By 1939 the foundations for the development of modern organosilicon chemistry had been laid.[1] Since then organosilicon chemistry has experienced a tremendous growth, due primarily to the commercial development of silicone rubber which was so important during World War II. Today, the commercial importance of silicone polymers is unquestioned, but basic research involving silicon has turned increasingly toward carbon-functional organosilicon compounds.

Both the electronic configurations of silicon and carbon (--- ns^2, np^2) and their respective positions in the periodic table (Group IVB) immediately suggest a similarity in the chemistry of the two elements. That they exhibit congenerous behavior is exemplified by the ability of both elements to catenate and to form tetracovalent species. Because of the previous development of carbon chemistry, it was inevitable that attempts would be made to force silicon into the framework of classical organic chemistry. It was soon apparent, however, that the "inevitable" was to fail and Rochow pointed out in 1951 that one should not be tempted to "... predict the reactions of silicon purely by analogy with carbon compounds."[2] Indeed, if organosilicon compounds were merely imitations of the analogous

carbon systems, organosilicon chemistry could not enjoy the prominence it has today. It is, in fact, the differentiating properties of carbon and silicon which warrant the greatest attention. An examination of some fundamental properties of these elements (Table 1-1) immediately reveals that substantial differences exist between them.

Table 1-1

Some fundamental properties of carbon and silicon

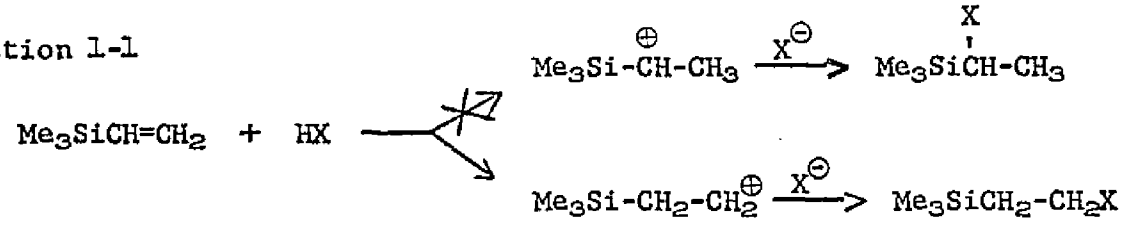
	C	Si
Atomic Weight	12.01	28.09
Atomic Radius, Å	0.772	1.176
1st ionization energy; K cal/g-atom	259.8	187.9
Electron affinity K cal/g-atom	28.8	33.7
Electronegativity (Pauling Scale)	2.5	1.8

As mentioned previously, the study of carbon-functional organosilanes is of considerable interest today. The majority of these compounds show significant deviations (to be discussed shortly) from the analogous compounds of carbon. The method most generally used to study these differences involves the preparation of two systems, i.e., an all carbon system and an analogous system containing a silicon atom. The two systems are then subjected to identical reaction conditions and any anomalous behaviour of the silicon compound (the carbon system is expected to behave "normally") is then assumed

to be caused either directly or indirectly by the presence of the silicon atom. In most instances any "anomalous" behaviour of the silicon system can be explained by (1) the low electronegativity of silicon relative to carbon, (2) the large size of the silicon atom relative to carbon, and (3) the availability of energetically low lying, empty d orbitals on the silicon atom.

An examination of the literature concerning organosilicon chemistry reveals significant differences in the chemistry of carbon-functional organosilanes and related all-carbon systems. The work to be presented in this dissertation involves the study of the anomalous and unexplained effect of the triorganosilyl moiety on adjacent electron deficient centers. This effect is exemplified by the non-Marcownicoff direction of addition of hydrogen halides under ionic conditions to vinylsilanes[3] (Reaction 1-1). That the trimethylsilyl moiety appears to adversely affect the stability of

Reaction 1-1



adjacent cationic centers is not uncommon in electrophilic reactions such as Reaction 1-1. In spite of these observations, it is commonly assumed in discussions of the reactivity of organosilanes[1] that the trimethylsilyl group has a strong inductive electron donating effect which would be expected to stabilize an adjacent cationic center. The contradiction noted here is the basis for this work.

Before studying the effect of the α-silyl group on adjacent electron deficient centers in detail, it will be useful to consider the reactions of alkylsilanes with functional groups β to silicon,[4] since observations such as that embodied in Reaction 1-1 contrast reactivity at positions α and β to silicon. β-Functional organosilanes have also been shown to undergo reactions which differ significantly from their carbon counterparts. For example, β-chloroethyltriethylsilane undergoes elimination of alkene in the presence of alkali[5] (Reaction 1-2).

Reaction 1-2

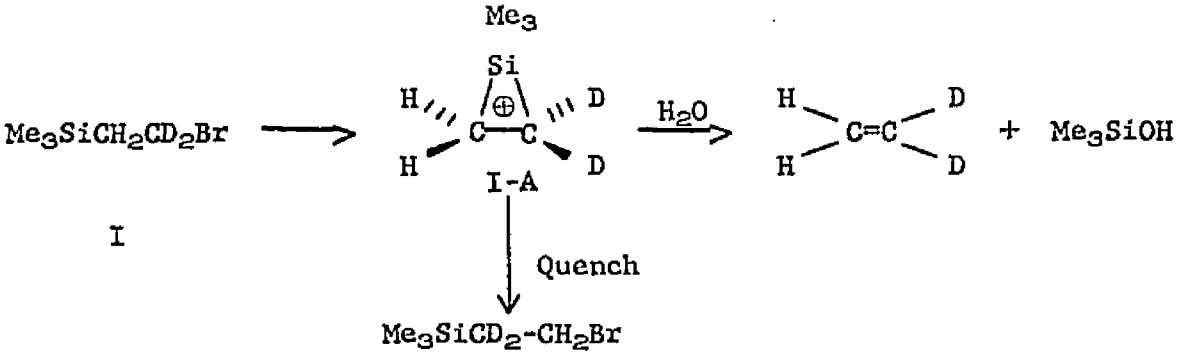
$$Et_3Si\text{-}CH_2CH_2Cl + {}^{-}OH \rightarrow CH_2{=}CH_2 + Et_3SiOH + HCl$$

The fact that the β-silicon atom is attacked by hydroxide ion in preference to the β-hydrogens is in sharp contrast to the analogous carbon system where the dehydrohalogenation product is observed.[6] In reactions with nucleophilic reagents in general, β-halogenoalkylsilanes have been shown to react much more rapidly than similar carbon systems, but also by different pathways (Reaction 1-2).

Sommer and Baughman[7] studied the kinetics of the solvolysis of β-chloroethyltrimethylsilane in aqueous alcohol and found that the reaction showed about the same sensitivity to the ionizing power of the solvent as the solvolysis of t-butyl chloride. Baughman[8] later

suggested that the initial step in the reaction involved the rate-determining cleavage of the carbon-halogen bond with assistance from the β-silicon group. Recently, Cook, Eaborn, and Walton[9] have studied the kinetics of solvolysis of deuterated β-chloroalkylsilanes (Reaction 1-3). They found that if the reaction is quenched after one half-life, rearranged starting material could be recovered. The

Reaction 1-3



deuterated compound, I, was used as evidence that anchimeric assistance by the trimethylsilyl group was involved. An intermediate such as I-A would be expected to lead to rearranged starting material. As further evidence that anchimeric assistance is involved, the authors then tried to show that Reaction 1-1 proceeded at a much faster rate than would be expected in the absence of direct participation. From $\sigma_p^{\oplus}$ constants determined in ionization reactions leading to the species, X-  -$CH_2^{\oplus}$, they predicted that 2-chloroethyltrimethylsilane is about $10^{3.5}$ times more reactive than methyl chloride under S_N1 conditions ($\sigma_p^{\oplus}$ for $(CH_3)_3SiCH_2$- = -0.50). If a linear free energy relationship

can be assumed to exist in this case, then the stabilizing effect of the $(CH_3)_3SiCH_2$- group on a carbonium ion intermediate should be less than that of two methyl groups ($\sigma_p^{\oplus}$ for Me = -0.31) and, therefore, 2-chloroethyltrimethylsilane should react slower than isopropyl chloride. However, it was found experimentally that the β-silyl chloride reacted about 10^5 times faster than isopropyl chloride. Even though the authors admit that the use of $\sigma_p^{\oplus}$ values and the assumption that a linear free energy relationship does exist in this particular case represents a "very rough" approximation, neighboring group assistance of some sort seems a reasonable postulate. It must be pointed out that β-halogenoalkylsilanes behave "normally" when compared to the β-halogen compounds of Group IV elements other than carbon (Reaction 1-4).[10]

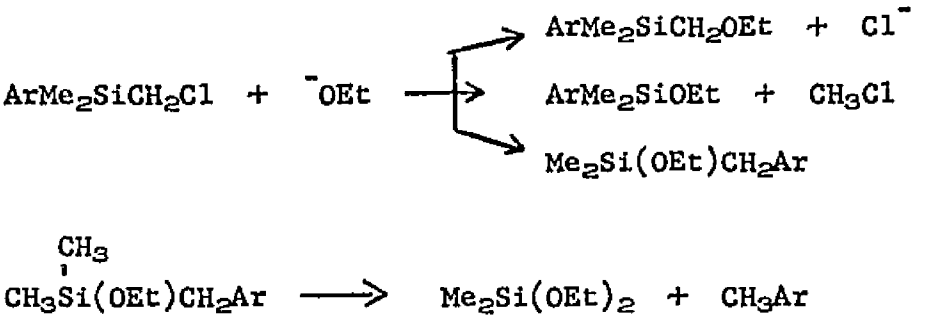
Reaction 1-4

$$X\text{-}CH_2CH_2GeX_3 + NaOH \rightarrow CH_2{=}CH_2 + GeCl_3X$$

In contrast to the reactions of β-halogenoalkylsilanes, the α-halogenated silanes seem to behave quite normally in comparison with similarly halogenated carbon compounds when subjected to reaction with nucleophiles under conditions which would be expected to lead to displacement through a bimolecular (S_N2) mechanism. For example, chloromethyltrimethylsilane is less reactive then n-hexylchloride[11] but more reactive than neopentylchloride[11] in the presence of ethoxide ion in ethanol. The relatively small

differences in rate seem reasonable, since steric hinderance to the attacking nucleophile is greater in neopentylchloride and much less in the unbranched alkyl chloride than in the α-halosilane. Even though steric effects can successfully explain the various rate differences under S_N2 conditions, Eaborn[1,5] has chosen to invoke other reasoning to explain the various rate data. He found that electron withdrawing groups attached to the silicon facilitate the displacement of halide by the nucleophile. For example, the compound $Me_3SiOSiMe_2CH_2Cl$ is more reactive than Me_3SiCH_2Cl in the presence of ethoxide ion; although the reaction is complicated by the cleavage of the $Si-CH_2Cl$ bond in the disiloxane.[12] Because of the effect of electron withdrawing groups on the reaction rate in nucleophilic reactions, Eaborn[1] proposed that the inductive release of electrons from the trimethylsilyl group creates an increased amount of electron density at the α-carbon which repels the attacking nucleophile, thereby decreasing the reaction rate. Additional evidence for this effect was obtained from the reaction of p-substituted aryl(chloromethyl)dimethylsilanes, p-$X-C_6H_4Me_2SiCH_2Cl$, with sodium ethoxide in ethanol.[5] The rate of this reaction was slowed by electron releasing substituents (X = p-Me, p-MeO-) and facilitated by electron withdrawing groups (X = p-Cl). However, it should be noted that along with substitution products, rearrangement and cleavage products were also obtained (Reaction 1-5).

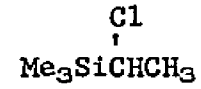
Reaction 1-5



It is also of interest that β-arylethylchlorides, when reacted under similar conditions with the same nucleophile are affected in the same way by electron withdrawing substituents on the phenyl ring, the ρ value for the reaction being 0.59. In fact, it is not at all uncommon for electron withdrawing substituents to increase the reaction rates for S_N2 reactions.[9]

If Eaborn is correct in his proposal that the inductive release of electrons by the trimethylsilyl group is great enough to repel an attacking nucleophile, then the effect that the trimethylsilyl group has on the reactivity of an adjacent carbon-halogen bond toward electrophilic reagents is truly an anomaly. Neither the chloride (Me_3SiCH_2Cl) nor the iodide (Me_3SiCH_2I) reacts with refluxing ethanolic silver nitrate under the same conditions which produce copious precipitates of the silver halide in similar primary alkyl halides. The positive inductive effect of the trimethylsilyl group would be expected to increase the reactivity of the α-halosilanes by stabilizing the incipient carbonium ion formed in the transition state leading to

the product. Similar reactivities are found when the reaction rates of organosilyl-substituted secondary chlorides (III) are compared with the rates of sec-butyl chlorides in the presence of electrophilic reagents. The organosilyl secondary halides do react in the presence of $AgNO_3$ but are less reactive than the corresponding organic halide.[14]

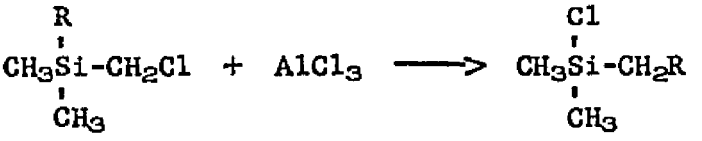


III

It has also been found that the tertiary α-halosilane, 2-bromo-2-trimethylsilylpropane, reacts very rapidly with silver perchlorate in carbon disulfide at room temperature.[15] It seems reasonable to infer from the relative reactivities of primary, secondary, and tertiary α-halosilanes that the silyl entity destabilizes the carbonium ion in the primary α-halosilane to such an extent that it cannot form. However, the addition of two methyl groups adjacent to the reaction center stabilizes the incipient carbonium ion, and the reaction proceeds vigorously. The possible reason for the destabilizing effect of the trimethylsilyl groups toward carbonium ion formation will be discussed in Chapter II.

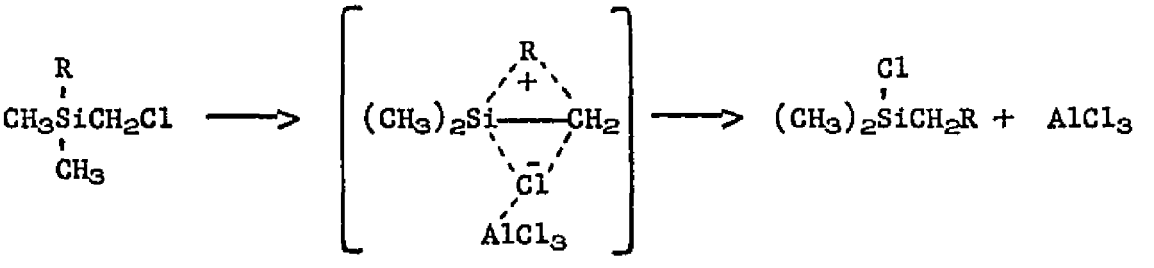
In contrast to the reactions with silver nitrate, the facile rearrangement reactions of α-halosilanes with Lewis acids have been extensively investigated.[16,17] The general reaction scheme is shown in Reaction 1-6.

Reaction 1-6



Originally the mechanism of Reaction 1-6 was thought to involve a carbonium ion-like transition state analogous to the Wagner-Meerwein rearrangements (see Chapter III) so common in organic chemistry.[16] After carrying out kinetic and structure-reactivity studies, Eaborn concluded that Reaction 1-6 proceeds through a concerted mechanism involving synchronous nucleophilic attack at silicon, migration of the organic group with its electron pair, and separation of the chloride ion from carbon which is under electrophilic attack by the aluminum chloride[1] (Reaction 1-7).

Reaction 1-7



IV

Later studies involving the relative migratory aptitudes of various alkyl groups[19] in the same rearrangement reaction shown in Reaction 1-6, led the authors to conclude that the migration of the alkyl group (R) from silicon to carbon is facilitated by electron releasing R groups.

That electron release increases the migratory aptitude of the organic group is a good indication that the transition state (or intermediate) IV involves a concentration of positive charge. Since the trialkylsilyl group apparently destabilizes an adjacent positive charge, there must be some factor involved in the Lewis acid catalyzed rearrangement reaction which can overcome this destabilizing effect, for the $AlCl_3$ reaction proceeds with ease at room temperature. That factor is probably the formation of intermediate IV (not likely in the $AgNO_3$ reaction) which lowers the transition state energy to overcome the adverse effect of the trimethylsilyl group.

It is the intent of the work to be presented herein to gain a better understanding of the effect of the trimethylsilyl group upon adjacent cationic centers. Significant conclusions concerning the role of alkyl groups in stabilizing adjacent carbonium ions will also be made.

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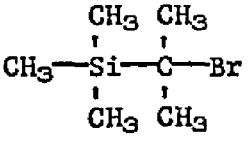
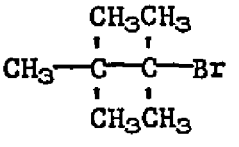
CHAPTER II

The literature is devoid of a systematic study of any tertiary α-halogenoalkylsilyl compounds and their solvolysis rates under S_N1 conditions. It is surprising that this should be the case, since there are ambiguities in the literature with respect to the effects of silyl entities upon cationic centers to which they are adjacent.[1] A systematic study of a tertiary system of this type would seem an important first approach in rationalizing the substituent effect of the silyl group on a more quantitative basis. The tertiary system I was chosen because it is a system very likely to undergo initial ionization under common S_N1 solvolysis conditions. An analogous carbon system II was prepared to be used as a model of normal



I



II

S_N1 reactivity. Compounds I and II were reacted under identical conditions and their absolute rates compared.

Whenever a comparison of solvolysis rates is made, it must be shown beyond reasonable doubt that both reactions are following similar reaction paths. If such is not the case, i.e., if different mechanistic pathways are involved, then any quantitative comparison

between the reaction rates of the two systems is of questionable validity. It is, therefore, not without reason that considerable time and effort has been spent in showing that compound I proceeds through an initial ionization mechanism to a transition state having a considerable amount of positive charge. Since compound II is generally considered to travel a similar reaction path,[2] conclusions concerning the mode of stabilization of carbonium ions by both alkyl and silyl moieties drawn from comparing the solvolysis rates of I and II will be valid.

There is rarely, if ever, a single experiment which can conclusively prove whether or not a specific mechanism is occurring in a solvolysis reaction. The procedure generally followed to elucidate a mechanism is to perform a series of experiments on a given substrate and to draw mechanistic conclusions on the basis of the sum of experimental data. With this in mind, five basic experiments were conducted with compound I to determine its mode of reaction. The first of such experiments involved the solvolysis of I in the presence of an added salt, LiBr (0.10 M in 0.019 M silane). In S_N1 reactions one of two forms of behaviour is normally observed on the addition of a common ion. One of these effects is rate retarding in nature and can occur when "free" ions are generated in the reaction media as shown in Reaction 2-1. The addition of common ion, X^-, shifts the

Reaction 2-1

$$RX \rightleftarrows R^+ + X^-$$

equilibrium to the left, thus effecting a decrease in the rate of reaction of R^+ leading to product.[3] The other form of behaviour commonly observed on the addition of common ion involves an increase in the reaction rate. The increase occurs when contact ion pairs are formed in the solvolysis medium (Reaction 2-2). The only observable effect of the added salt in Reaction 2-2 is to increase the ionic

Reaction 2-2

$$RX \rightleftharpoons [R^+ X^-]$$

strength of the solvent and thus increase the rate of ionization. For example, a slight increase in rate due to added salt has been shown to occur in the solvolysis of t-butyl bromide when reacted in the presence of 0.10 M LiBr ($k/k^o = 1.41$).[4] It was found experimentally that the rate was also slightly increased for I ($k/k^o = 1.1$).

The second reaction carried out on the silyl substrate for mechanistic determination was solvolysis in the presence of added base, NaOH (0.03M in 0.012M silane). If a simple rate-determining ionization process is occurring, the results should be similar to that obtained when the reaction was carried out in the presence of added salt.[4] If a bimolecular process is occurring, the rate of the reaction should be sharply enhanced[5] by the base since a highly nucleophilic entity has been added. Experimentally it was found that for the silyl substrate, I, the rate was increased only slightly ($k/k^o = 1.4$).

The results of these first two experiments are indicative of a rate-determining ionization process.

One of the most convincing lines of evidence which can differentiate between unimolecular and bimolecular reactions was first developed by Grunwald and Winstein.[6] They reasoned that since a unimolecular reaction proceeds through a rate-determining ionization process to a cationic intermediate, the rate of this ionization process should in some measurable way be quantitatively dependent upon the ionizing power of the solvent in which the reaction is carried out. With this in mind they developed the empirical linear free energy relationship,

$$\log k = mY + \log k_o$$

In this equation 'm' is a constant characteristic of the substrate, and measures the sensitivity of the solvolysis rate to the ionizing power of the solvent. Y is a parameter representing the ionizing power of the specific solvent used relative to the standard solvent, 80 volume % aqueous ethanol (Y = 0). The rate constant, k_o, is defined as the rate constant for a given substrate in the standard solvent and k is the reaction rate of the substrate in any solvent. t-Butyl chloride was chosen as the standard substrate and given an arbitrary value of m = 1. t-Butyl chloride was chosen to represent the limiting case for an S_N1 type ionization. That t-butyl chloride

was a reasonable choice for representing S_N1 reactions has been confirmed by comparison with other systems generally considered to proceed with initial ionization (Table 2-2) and, more recently, by results of experiments on bridgehead systems[7] where nucleophilic participation is not possible for steric reasons. The silyl substrate (I) was subjected to this diagnostic test for mechanistic path by carrying out the solvolysis of I in solvents of varying Y values (Table 2-1) and graphically plotting log k versus Y (Figure 2-1). The m value for the silyl substrate can be determined by calculating the log k versus Y slope from the graph. The m value determined in this manner for the silyl substrate is 0.66 (slope determined by the method of least squares). From Table 2-2 it can be seen that this m value

Table 2-1

Solvolysis[a] in solvents of varying Y values

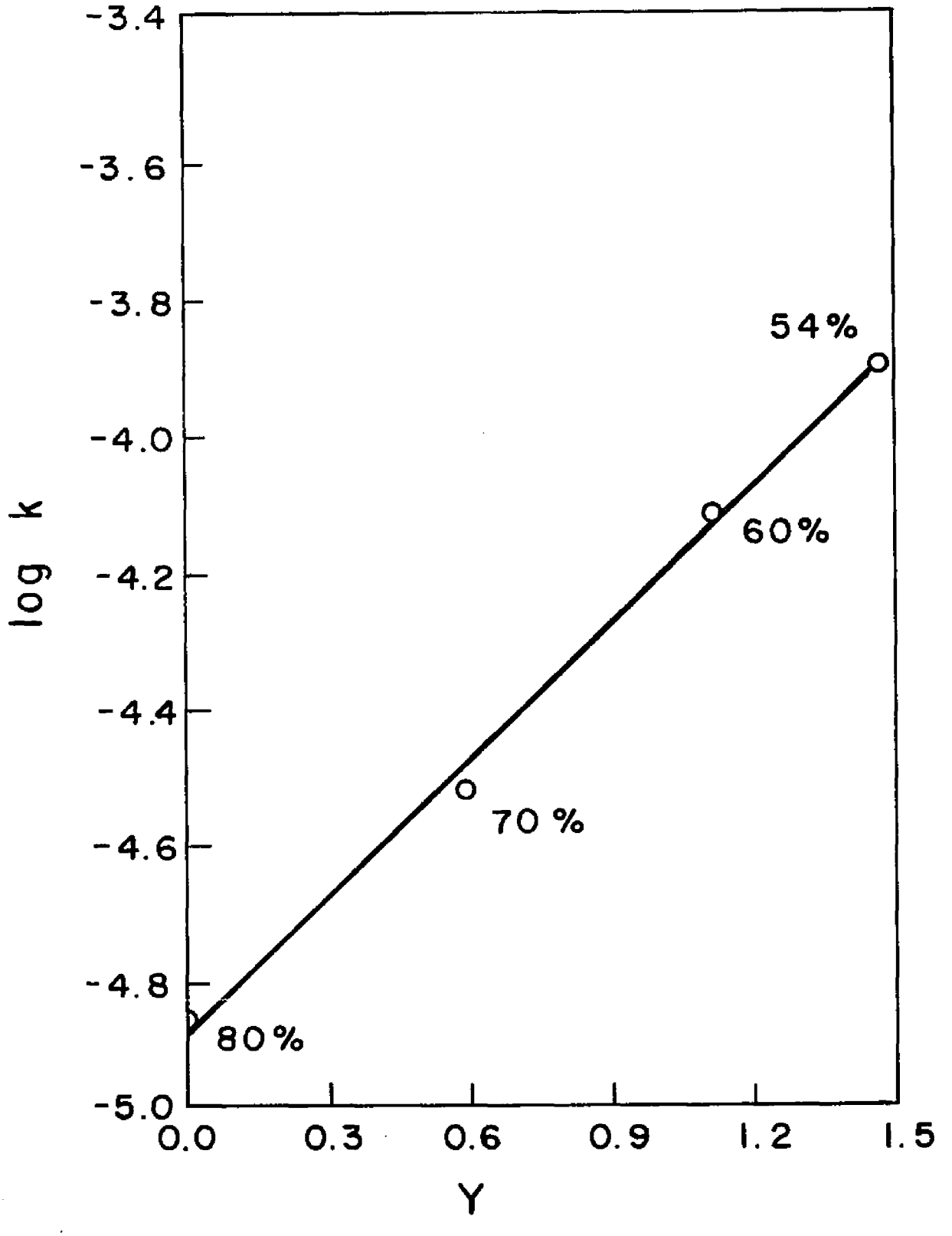
Solvent	Added Salt	k x 10^5, sec^{-1}	k rel
54% EtOH/H_2O	---	10.5	1
60% EtOH/H_2O	---	6.44	.61
70% EtOH/H_2O	---	2.53	.24
80% EtOH/H_2O	---	1.16	.11
54% EtOH/H_2O	0.03 M NaOH	14.6	1.4
65% MeOH/H_2O	---	14.6	1
65% MeOH/H_2O	0.10 M LiBr	16.1	1.1

[a] at 80°

compares quite favorably with the m value of substrates which are generally considered to undergo solvolysis through an initial rate-determining ionization.

Figure 2-1

log k versus Y. Rate Constants for 2-Bromo-2-trimethylsilylpropane Determined in Varying Compositions of Aqueous Ethanol. Percentages are volume percent water in ethanol.


-3.4
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
-4.8
-5.0
log k
0.0
0.3
0.6
0.9
1.2
1.5
Y
54%
60%
70 %
80%

The fourth experiment to be carried out on compound I, and one often overlooked in kinetic studies, was the determination of the reaction products. This represents a crucial experiment since it is not uncommon in nucleophilic reactions involving silicon for the

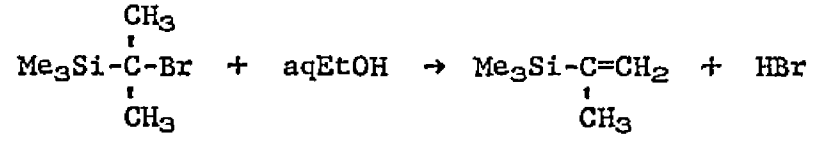
Table 2-2

Average Values of m Obtained in Various Solvents

Compound	m value[7a]
t-Butyl chloride	1.00
Neopentylbromide	0.71
α-Methylneopentylbrosylate	0.71
Benzhydryl chloride	0.76
2-Bromo-2-trimethylsilylpropane	0.66

nucleophile to attack the silicon atom to yield various siloxanes.[1] When I was refluxed in 80% ethanol for 4 days, the only detectable reaction product was trimethylisopropenylsilane (Reaction 2-3).

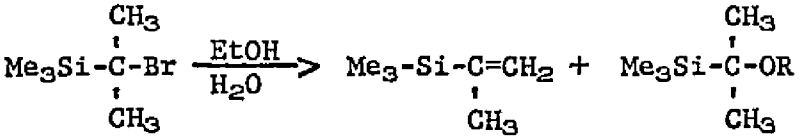
Reaction 2-3



That only one product is produced in Reaction 2-3 is unexpected since in the solvolysis of II, the substitution product was isolated in addition to elimination product.[8] It is possible that some of the

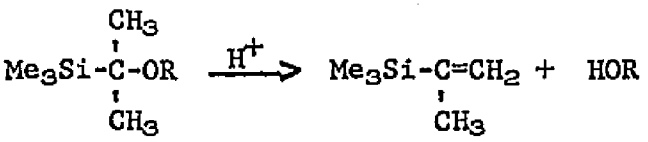
substitution products were formed initially but were then rapidly cleaved by the HBr as shown in Reactions 2-4 and 2-5.[2] There is no indication that Reaction 2-5 is actually occurring. Since the ether

Reaction 2-4



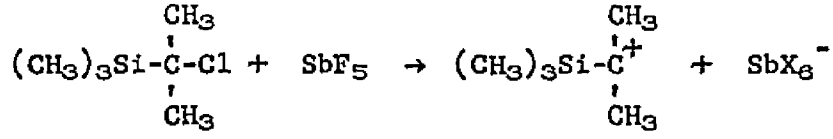
R = H, OEt

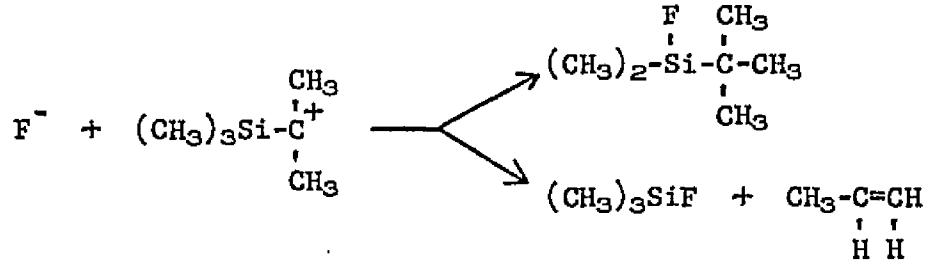
Reaction 2-5



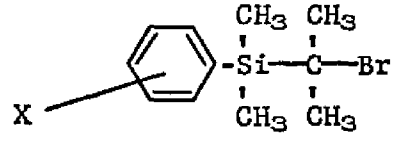
(R = Et in Reaction 2-5) would not be expected to cleave readily[9] under the reaction conditions prevailing in this reaction it would probably have been detected if formed to any degree. It is interesting that O'Brien[10] obtained different products when he generated a carbonium ion similar to that formed in Reaction 2-3 in a non-nucleophilic medium (Reaction 2-6).

Reaction 2-6





The fifth experiment which was performed in order to elucidate the mechanistic details of the solvolysis of I involved a series of compounds of the general structure shown in III. Each of these



III

substrates was reacted under the identical solvolytic conditions in which compound I was reacted. The data are recorded in Table 2-3.

Table 2-3

Rate Constants for Solvolysis of Arylsilanes (III)

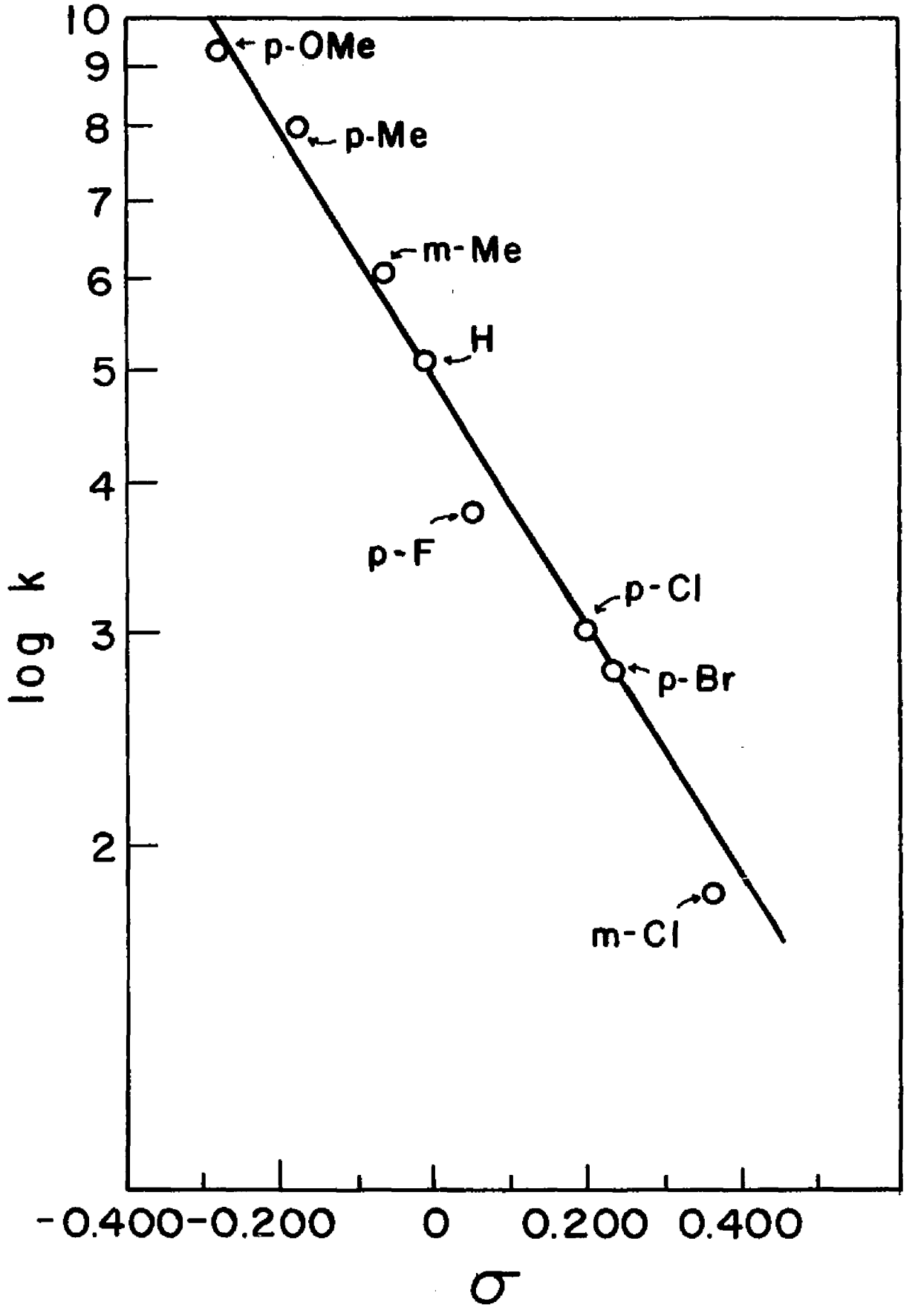
Obtained in 54 Volume % Aqueous Ethanol at 80°.

Substituent (X)	k average x 10^5, sec^{-1}	σ values[12]
p - OMe	9.58	-0.268
p - Me	7.51	-0.170
m - Me	6.06	-0.069
H	5.09	0.000
p - F	3.88	0.062
p - Cl	3.05	0.227
p - Br	2.86	0.232
m - Cl	1.83	0.373

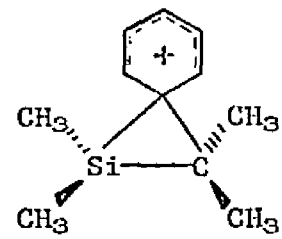
It is readily noticeable that none of the different groups (X) exerts a sizable effect on the reaction rate. This is not totally unexpected since there is a rather large distance between the reaction center and the point of substitution. A Hammett plot[12] of log k versus σ was made, and the data were found to correlate very well with σ (Figure 2-2). The ρ value was determined from the slope of the log k versus σ plot by the method of least squares and found to be -1.14. Since the data correlate with σ, the transmission of electrical effects is apparently "normal", i.e., anchimeric assistance from the phenyl group as shown in the possible intermediate IIIA is apparently absent. If a neighboring group effect were present, a sharp deviation[8] would be expected in the log k versus σ plot (Figure 2-2) especially in the case of the para-methoxy substituent which is the best electron donor and the most likely group to give anchimeric assistance. A neighboring group

Figure 2-2

log k versus σ. Rate Constants for the 2-Bromo-2-(aryldimethylsilyl)-propanes Obtained in 54 Volume % Aqueous Ethanol

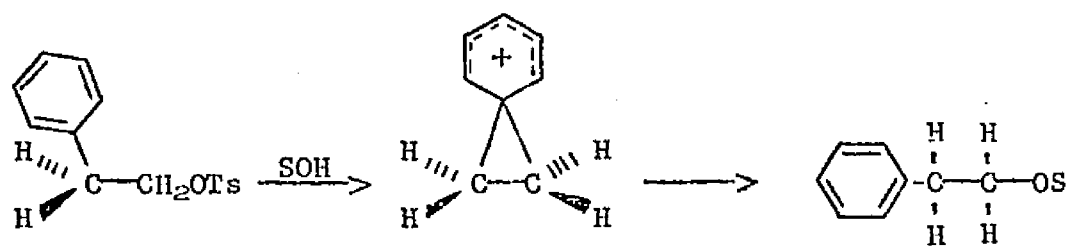

10
9
8
7
6
5
4
3
2
log k
p-OMe
p-Me
m-Me
H
p-F
p-Cl
p-Br
m-Cl
-0.400
-0.200
0
0.200
0.400
σ

effect involving a bridged cation is commonly proposed in solvolytic displacement reactions at carbon in β-phenylethyl derivatives[13] as shown in reaction 2-7 and also for $AlCl_3$ catalyzed rearrangements of

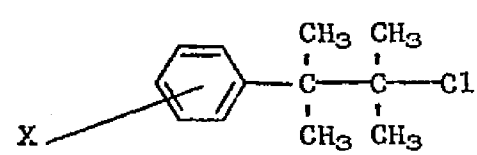


IIIA

Reaction 2-7



(α-haloalkyl) arylsilanes[14,15] (See Chapter I). Brown and Kim[8] have reported the solvolysis of V in 80% aqueous ethanol and found results similar to that for compound III in that substituents on the phenyl group affect the rate only slightly (Table 2-4). However, Brown



V

Table 2-4

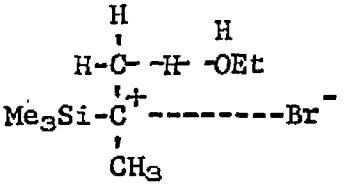
Relative substituent effects

Substituent (X)	k rel V	k rel III
H	1.00	1.00
m - Me	1.44	1.20
p - Me	2.51	1.60
p - OMe	7.86	2.00

interprets his data in terms of weak through-space interactions between the aromatic ring and the developing cationic center. The argument is based on the single observation that the para-methoxy derivative shows some deviation from the Hammett plot. The para-methoxyphenyl group would be the one most likely to give significant anchimeric assistance. The results obtained from the solvolysis of III do not justify such an interpretation for III. In the series of silyl derivatives there is a good correlation with σ constants even with a good electron donor such as para-methoxy. That anchimeric assistance is not observed in the solvolysis of III could be due to the fact that the large size of the silicon atom and the long silicon-carbon bond length prevent any through-space interaction between the ion being formed in the ionization process and the phenyl ring.

Since the ρ value for III is negative, it would appear that it is correct to picture a substantial amount of positive charge developing in the transition state during the solvolysis reaction.[16] In fact, all of the experiments done on I thus far indicate that the solvolysis mechanism involves a transition state which has considerable

carbonium ion character. However, since the only silane product formed upon the solvolysis of I is trimethylisopropenylsilane, the mechanism is considered to be bimolecular in character with at least some C-H bond breaking having occurred at the transition state in addition to considerable C-Br bond breaking. If a simple ionization process were



VI

occurring during the solvolysis of I, it would seem reasonable to expect some of the substitution product to be formed. Steric hindrance to attack at carbon in a carbonium ion intermediate is believed to be a major factor in promoting elimination, involving attack at a less hindered H atom, at the expense of substitution. Since the carbon analog II does give substitution, the less hindered silane I ought reasonably to give some substitution also, unless there is at least some minor difference in solvolysis mechanism between I and II. It seems reasonable to postulate that the minor mechanistic difference in the solvolyses of I and II is the small degree of solvent participation shown in VI.

Even though the mechanism is considered bimolecular in nature, the rate-determining step involves the formation of a substantially

electron deficient carbon atom, and therefore, the comparison of the solvolysis data of I and II is justified. The absolute and relative rates of I and II are shown in Tables 2-5 and 2-6, respectively, along with the relative rates of some related compounds.

Table 2-5

Summary of Solvolysis Data Obtained in 54 Volume % Aqueous Ethanol

Compound	10^5 k, sec^{-1}					$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	25°[a]	50°	70°	80°	85°	kcal/mole	eu
I	.016	.34	4.15	10.5	24	27.0	-1.2
	-9°	2°	15°	25°			
II	3.7	32	167	610		21.7	+2.0

[a]Extrapolated value from the four rates at higher temperature.

Table 2-6

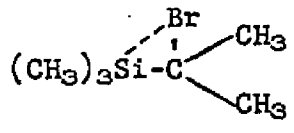
Relative Rates

Compound	k_{rel}, 25°
I	1
II	38,000
$(CH_3)_3C$-Br	19,000[18]
$(CH_3)_2HC$-Br	1

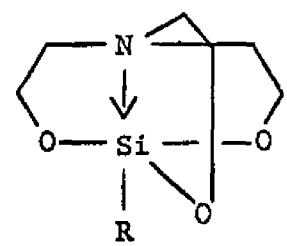
From the data presented in Tables 2-5 and 2-6 the tremendous rate difference between I and II can clearly be seen (k_{II}/k_I = 38,000). A number of factors are certainly involved in determining the relative rates of I and II, and probably the most obvious one is the expected

steric acceleration in going from I to II due to the shorter bond lengths in II. The shorter bond lengths in II produce severe non-bonded interactions between the bromine and the methyl groups which can be relieved in the transition state which is approaching a planar carbonium ion. The relief of steric strain in going to the transition state should produce a lower activation energy for II relative to I. It is not possible to quantitatively predict the magnitude of steric acceleration in this particular instance, but Brown[17] has made the significant observation that II undergoes solvolysis at a rate faster than t-butyl bromide by a factor of only 2 (Table 2-7). t-Butyl bromide may or may not be a good model for I, but t-butyl bromide is substantially less sterically crowded than II. It thus seems inconceivable that the rate difference of 38,000 between I and II could in any large measure be due to steric factors alone.

For I there also exists the possibility of a 1,3-interaction between the lone pairs of electrons on bromine and the empty d orbitals of silicon (I-A) which could materially effect the rate of solvolysis of I. An interaction involving donation of non-bonding electrons into



I-A



VII

the empty d orbitals of silicon (VII) is well-documented in the literature.[18,19,20] Although the idea of a 1,3-interaction has not been ruled out completely in the case of I, experimental evidence obtained thus far indicates that if a 1,3-interaction does exist, it is relatively minor. For example, infrared data involving the carbon-bromine bond stretch (Table 2-7) seem to indicate that there is no particular ground state stabilization in the silyl system relative to the all carbon system. The increased carbon-bromine bond stretching

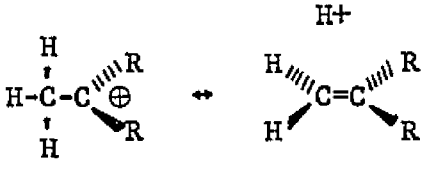
Table 2-7

Compound	ν_{C-Br}, cm^{-1}	$\Delta S^{\ddagger}$, eu
I	584	-1.2
II	550	+2.6

frequency may well be due to first, the previously discussed steric effect which, due to the longer carbon-silicon bond lengths in I relative to II, is less in I than II, thus producing a shorter and stronger carbon-bromine bond in I. Another piece of evidence which makes a 1,3-interaction seem doubtful is the value of the entropy of activation for the silyl substrate (Table 2-7). If a 1,3-interaction were involved, the entropy of activation might be expected to be more positive for I than for II, since the restriction of rotation in the ground state due to this interaction would be relieved in going to the transition state. A third piece of evidence which disfavors a 1,3-interaction between bromine and silicon lies in the fact that

silicon is a poor Lewis acid, and all known examples of expanded coordination have highly electronegative substituents attached directly to the silicon atom (see VII).

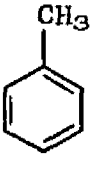
Thus, the experimental data seem to eliminate the obvious possibilities for explaining the rate differences between I and II, i.e., significant differences in mechanisms of solvolysis, non-bonded steric interactions between bromine and the methyl groups, and a 1,3-interaction between bromine and silicon. A logical explanation which can explain the observed rate differences between I and II can be stated in terms of the differences in hyperconjugative effects between a trimethylsilyl and a t-butyl group adjacent to a developing carbonium ion center. Hyperconjugation, which may be represented in valence bond terms as in VIII, is generally accepted to be a highly stabilizing factor when an alkyl group is adjacent to a cationic center.[21] However, in the case of the trimethylsilyl group, the



VIII

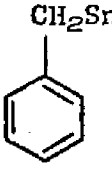
longer carbon-silicon bond lengths and probably other factors as well, such as displacement of electron density more toward carbon in the carbon-silicon bond, make significant interaction of the empty p orbital on the carbonium ion center and the sigma electrons of the

methyl-silicon bond unfavorable. If a resonance interaction, i.e., hyperconjugation, is not available to the silyl system, then the only alternative of the trimethylsilyl group to stabilize an adjacent positive charge is that of induction. Based upon the electronegativity values of carbon and silicon (see Table 1-1), it must be predicted that a positive inductive effect would be greater for the trimethylsilyl group than for the t-butyl group. The lower value of electronegativity for Si should lead to an acceleration of the ionization of I relative to II. Recent data published by Traylor;[22] however, seem to indicate that the inductive effect of the trimethylsilyl group is minor. Traylor draws this conclusion from observing charge-transfer spectra of complexes of TCNE and various aromatic systems to which some organometallic group, such as, $-SnMe_3$, -HgCl, $-SiMe_3$, etc., was attached. He found that when the carbon-metal bond was free to interact in a hyperconjugative manner with the positively charged aromatic center, the absorption frequency was drastically reduced (IX and X). However, if the carbon-metal



24,300 cm^{-1}

IX



17,500 cm^{-1}

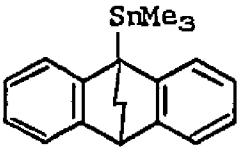
X

bond were forced to remain in the plane of the aromatic ring, the only interaction which could ensue would be one of induction (XI, XII).

For example, the only effect which can be exerted by the -$SnMe_3$ group in XII is an inductive effect, since for a hyperconjugative effect to

23,600 cm^{-1}

XI



23,600 cm^{-1}

XII

be operative (as for that matter, any type of π conjugation), the coplanarity of the carbon-metal bond and the axis of the pi orbital of the aromatic rings is required. In this latter case, no frequency shift is observed. Therefore, Traylor concludes that "the inductive effects of metallic group, MR_3, in the -CH_2MR_n group are negligibly small."

There is no way available in our system at present to assess the inductive effect of the trimethylsilyl group quantitatively because of factors to be discussed shortly. It can be said, however, that the inductive effect appears to be a minor factor here also, and in a system which should be demanding inductive stabilization. This conclusion can be drawn from a comparison of the solvolysis rates of I and isopropyl bromide; although from the work of Schleyer[23] it is realized that there are many complications in interpreting rate data in secondary alkyl systems. Since the rates of reaction of I and

isopropyl bromide are equal under identical reaction conditions, it is tempting to compare directly the abilities of H and the trimethylsilyl group in stabilizing an adjacent carbonium ion. This direct comparison is not possible since the rate for isopropyl bromide is certainly solvent assisted, and probably to a much greater degree than is I. This solvent assistance is revealed by the respective m values for these two substrates:

Isopropyl bromide	m = 0.43
2-Bromo-2-trimethylsilylpropane	m = 0.66

It cannot be concluded then, from the rate data alone, that the trimethylsilyl group is no better at stabilizing a carbonium ion than is hydrogen. However, the trimethylsilyl group does not appear to be a very significantly better electron donor than H, and it is certainly substantially poorer than a methyl group (from a comparison of the rates of I and t-butyl bromide). The comparison of isopropyl bromide and I does indicate that the inductive effect of the trimethylsilyl group is minor and, if such is the case, it seems only reasonable to conclude that the inductive effect of the more electronegative t-butyl group is even smaller. It appears that since I does not approach II in rate, the major effect afforded to the incipient carbonium ion by the t-butyl group is a hyperconjugative effect and the inductive effect is minor indeed. That hyperconjugation may be a major driving force in many reactions where carbonium ion products are formed is supported by these results even though conflicting views concerning the significance of hyperconjugation have been expressed.[24]

The rate data presented here are the first data available which allows a comparison of the ability of an alkyl group to stabilize an adjacent carbonium ion with the ability of a much more electropositive substituent. This type of system (I) is of importance since it affords the potential for giving a means of separating the hyperconjugative and inductive effects of alkyl substituents.

CHAPTER II

Experimental

General for All Chapters

Unless otherwise stated, all reactions were run in three-neck round bottom flasks equipped with a mechanical stirrer, reflux condenser, and an addition funnel. All glassware was flame dried and flushed with argon prior to conducting the experiment. In general the solvents were dried by refluxing over calcium hydride and distilled, with middle fractions from the distillations being used in the reactions. Where mixed solvents were used, the percent composition quoted is volume percent. Melting points were taken on a Drechsel melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained routinely on a Varian A60A, and infrared (IR) spectra were recorded using a Beckman IR-5. Mass spectral data were collected using a Varian M-66. The molecular weights quoted were determined by mass spectrometry.

Solvolysis of 2-Bromo-2-trimethylsilylpropane

2-Bromo-2-trimethylsilylpropane (3.86 g, 0.0198 mole) was placed in a 100 ml single-neck flask equipped with a reflux condenser which was connected to a CCl_4-Br_2 trap. To the flask was added 60 ml of 80% aqueous ethanol and this mixture was refluxed for 4 days. Daily monitoring of the CCl_4-Br_2 trap by NMR gave no indication that alkene was being evolved during the time of refluxing. To the reaction mixture was then added 20 ml of distilled water causing two layers to

form in the reaction flask. The NMR spectrum of the bottom layer indicated that only ethanol, water, and starting material were present. The whole mixture was added to a separatory funnel and the two layers were separated. The aqueous ethanol layer was washed 5 times with 10 ml portions of pentane and discarded. The pentane was placed over $CaCl_2$ overnight to dry. Distillation yielded approximately 0.60 grams of starting material and a very minute amount of isopropenyltrimethylsilane (identified by NMR but not isolated). It was apparent from the odor of the pentane that it still contained some of the starting material even after distillation. The top layer in the separatory funnel was placed over molecular sieves to dry. The NMR spectrum of this layer indicated it to be pure isopropenyltrimethylsilane[25] (1.10 g, 60%).

NMR Data:	Singlet	δ 0.07 (9H)
	Multiplet	δ 1.71-1.95 (3H)
	Broad Doublet	δ 5.35 (2H)

2-Bromo-2-trimethylsilylpropane

Lithium sand (4.26 g, 0.66 mole) was prepared by rapidly stirring a suspension of melted lithium in mineral oil at ca. 200°. The mixture was allowed to cool to room temperature and washed with dry pentane. The lithium was then placed in a 1000 ml three-neck flask equipped in the usual manner, along with 200 ml of dry pentane which prior to distillation had been stored over sulfuric acid. Freshly distilled 2-chloropropane (24.1 g, 0.33 mole) was placed in

the addition funnel and 5 ml was allowed to drain into the lithium-pentane solution to initiate the reaction. Once the reaction had started, 250 ml of the dry olefin-free pentane was added to the addition funnel and this solution was added to the lithium over a period of about 2 hours. After the addition was complete, the mixture was stirred for 2 hours and was immediately added via an addition funnel to neat trimethylchlorosilane (27 g, 0.25 mole) contained in a 500 ml three-neck flask equipped in the usual manner. The isopropyllithium was added to the silane over a period of about one hour and stirring was continued overnight. The reaction mixture was then hydrolyzed in a saturated aqueous solution of NH_4Cl, washed with water, and the pentane layer placed over $CaCl_2$ for 12 hours. The pentane was then removed with a Rinco rotoevaporator and the remaining material was distilled through a six inch Vigreaux column to yield the desired trimethylisopropylsilane (b.p. 87-88°/760mm, 15 g, 55% yield) (Literature 87°/737mm).[26]

In a 100 ml three-neck flask equipped in the usual manner was placed 3.42 g (0.029 mole) of trimethylisopropylsilane which was then heated to about 60°. Bromine (4.63 g. 0.029 mole) was then added via the addition funnel at such a rate as to maintain a light red solution. After the addition of bromine was complete, the solid was immediately sublimed under vacuum at room temperature. Pure product was obtained after twice subliming the silane. The yield of 2-bromo-2-trimethylsilylpropane was 3.46 g (64%), m.p. 121-123° in a

sealed tube. (Found: C, 36.78; H, 7.70; Si, 14.39%. Calcd. for $C_6H_{15}SiBr$: C, 36.92; H, 7.75; Si, 14.39%).

NMR Data:	Singlet	δ 0.12 (9H)
	Singlet	δ 1.70 (6H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	73	100
	194	< 1

Dimethyl-t-butylcarbinyl Bromide

t-Butyl chloride was prepared according to the method of Fieser and Fieser.[27] t-Butyl alcohol (2.5 moles, 183.5 g) was placed in a 2000 ml separatory funnel containing an excess of concentrated hydrochloric acid. The mixture was shaken for 10 minutes and the two layers allowed to separate completely. When the lower acid layer was clear, the two layers were separated with the t-butyl chloride layer being placed over $CaCl_2$ to dry. The chloride was used without further purification.

t-Butylmagnesium chloride was prepared in the usual manner by adding the previously prepared chloride (2.0 moles, 195 g) to an ethereal suspension of magnesium (48.6 g, 2.0 moles) in a one liter three-neck flask equipped in the usual manner. Stirring was continued for 2 hours after the addition was complete. The Grignard solution was then added directly to reagent grade acetone (2.0 moles, 116 g). After the Grignard solution had been added, the reaction mixture was

hydrolyzed in 600 ml of 2M hydrochloric acid to yield dimethyl-t-butylcarbinol. The ether was removed by a rotary evaporator, and without further purification the alcohol was allowed to react with concentrated hydrobromic acid (454 g of 48% aqueous HBr). The dimethyl-t-butylcarbinyl bromide precipitated from the solution, and the dark brown crystals were collected by suction filtration. The impure solid was immediately sublimed under vacuum at room temperature, and pure colorless crystals, m.p. 152-154° in a sealed tube (literature: 150-152°),[17] were obtained after the third sublimation. The yield was ca. 10%.

NMR Data:	Singlet	δ 1.13 (9H)
	Singlet	δ 1.80 (6H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	57	100
	99	95
	178 (parent peak)	0

Solvolysis Reactions

Materials. The substrates, dimethyl-t-butylcarbinyl bromide and 2-bromo-2-trimethylsilylpropane, were prepared and purified as previously described. The aqueous ethanol was prepared by mixing 60 volumes of 100% ethyl alcohol (reagent grade, used without further purification) and 40 volumes of distilled water. The density of the solution as determined by a Gay-Lussac pycnometer was 0.90412 g/ml.

For titration of the solvolysis mixture, appropriate quantities of sodium hydroxide were added to distilled water to yield an approximately 0.01M solution which was standardized against a 0.10M standard nitric acid solution.

Kinetic Measurements. A weighed quantity of the silyl halide (sufficient to yield a solution approximately 0.014M in substrate) was dissolved in 125 ml of aqueous ethanol. Portions of 5 ml were then pipetted into 5 ml ampoules which were sealed and placed in a constant temperature oil bath at 80.0 $\pm$ 0.1° maintained by a Sargent thermonitor. At definite time intervals an ampoule was removed from the bath and placed immediately in an ice bath to stop the reaction. The contents of the ampoule were then poured into 25 ml of absolute ethanol at 0°. The reactions were usually followed to at least 80% completion with generally 10 points determined per run. The HBr formed during the course of the reaction was titrated with the 0.01M sodium hydroxide using cresol red as the indicator. The original concentration of the halide was determined by letting the reaction proceed at 80° through about 10 half-lives and determining the amount of HBr produced in the usual manner. Agreement between calculated and found amount of HBr in the infinity titration was in each case within $\pm$ 0.2 ml or 2 to 3%.

The carbinyl halide reacted too rapidly to be sealed in an ampoule. The procedure used for the determination of these first order rate constants is a modification of the method used by Brown and co-workers.[17] In a 250 ml volumetric flask was placed 100 ml of the

60% ethanol solvent. The flask was immersed in a constant temperature bath until temperature equilibrium was attained (30-45 minutes). After this time a weighed quantity of the carbinyl halide (0.5 to 0.7 g) was dissolved in 5.0 ml of absolute ethanol and added immediately to the volumetric flask with the contents being mixed thoroughly by rapid swirling of the flask. At definite time intervals, 5.0 ml samples of the solution were pipetted out and run into 50 ml of absolute ethanol at 0° in order to halt the reaction. The titration of the acid produced was carried out in a manner exactly analogous to that for the silyl halide.

From the data obtained as described above the first order rate constants (k_1) could be calculated using the following equation:

$$k_1 = (2.303/t) \quad \log a/a-x$$

where 't' is the time in seconds, 'a' is the original concentration of the substrate, and 'a-x' is the concentration of substrate at time 't'. In practice the rate constants were usually determined graphically by plotting log (a-x) versus time and using a least squares computer program. Since the reaction is first order, the concentrations were expressed in ml of sodium hydroxide required for the titration of the 5 ml samples.

Solvolysis of 2-Bromo-2-trimethylsilylpropane in the Presence of Added Salt

To a 70% aqueous methanol solution of 2-bromo-2-trimethylsilylpropane was added enough LiBr to make the solution 0.1M

in LiBr. The rate constant was determined in the usual manner as previously described. The solvolysis was carried out in duplicate with nine points being determined for each run.

Solvolysis of 2-Bromo-2-trimethylsilylpropane in the Presence of Added Base

The same procedure was used as above except that enough sodium hydroxide was dissolved in 125 ml of 54% aqueous ethanol containing the silane to make a solution which was 0.03M in NaOH.

Arrhenius Parameters. The Arrhenius parameters for the two substrates were determined in the usual manner[28] by plotting log k versus 1/T. For both the silyl and carbinyl substrates rate constants were determined at four different temperatures.

Solvent Dependence Studies

The techniques employed for the determination of these particular rate constants have been described previously. The substrate, 2-bromo-2-trimethylsilylpropane, was solvolyzed in various solvents ranging in Y^6 values from 0.00 to 1.47. These Y values for each of the different solvents were those which had been determined previously by Winstein and co-workers.[29] A plot of log k (k being determined in each of the solvents) versus Y yielded a straight line for the aqueous ethanol system as shown in Figure 2-1. The slope of the log k versus Y plot represents the Winstein-Grunwald 'm' value for this substrate.

Chlorodimethylisopropylsilane

In a 500 ml three-neck flask equipped in the usual manner and containing neat dimethyldichlorosilane (0.50 mole, 64.5 g) was added isopropyllithium (0.50 mole as determined by acid titration) prepared as described previously. After the addition was complete, the mixture was stirred for two hours and then filtered under N_2 through a sintered glass cylindrical tube filter. The lithium chloride remaining in the filter was washed several times with dry pentane. The filtrate was then distilled through an 18 inch Vigreaux column until the pentane was removed, and the remaining mixture was distilled through a 6 inch Vigreaux column to yield chlorodimethylisopropylsilane, b.p. 110-112°/760mm (literature: 109.8-110°/738mm).[26] The yield was 37%.

2-Bromo-2-(chlorodimethylsilyl)propane

Chlorodimethylisopropylsilane (49 g, 0.36 mole) was brominated and purified in exactly the same manner as described for 2-bromo-2-trimethylsilylpropane. The yield of brominated product was 68.5 g, 91%. The NMR spectrum was recorded.

NMR Data:	Singlet	δ 0.38 (6H)
	Singlet	δ 1.60 (6H)

2-Bromo-2-(phenyldimethylsilyl)propane

A solution of phenyllithium was prepared in the usual manner by slowly adding an ethereal solution of bromobenzene (15.7 g, 0.10 mole) to a 500 ml three-neck flask equipped in the usual manner and

containing an ether suspension of lithium wire (1.47 g, 0.21 g atom) which was cut into small pieces (0.25 cm). After the addition of the bromobenzene was complete, the mixture was stirred for one hour and added immediately to the 2-bromo-2-(chlorodimethylsilyl)propane dissolved in ether and contained in a 500 ml three-neck flask equipped in the usual manner. The addition of the lithium reagent was complete in 30 minutes and the mixture was stirred for 2 hours. The reaction mixture was then added to an ice-cold solution of saturated aqueous ammonium chloride, washed with ice water, and the ether layer placed over $CaCl_2$ for 12 hours. The ether was then removed with a rotary evaporator and the residue distilled through an annular teflon spinning band column. Pure compound was collected at 110°-111°/5mm Hg. (Found: C, 51.65; H, 6.89%; mol. wt. 258. Calcd. for $C_{11}H_{17}SiBr$: C, 51.36; H, 6.66% mol. wt. 257.3). The yield of pure product was 12%. The total yield including slightly impure product was 60%. The NMR and mass spectral data were recorded.

NMR Data:	Singlet	δ 0.48 (6H)
	Singlet	δ 1.68 (6H)
	Multiplet	δ 7.20-7.69 (5H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	135	100
	199	5
	201	5
	258	< 1

2-Bromo-2-(p-tolyldimethylsilyl)propane

A solution of p-tolyllithium was prepared in a 500 ml three-neck flask equipped in the usual manner by adding an ethereal solution of p-bromotoluene (23.1 g, 0.135 mole) to an ether suspension of lithium sand (1.9 g, 0.27 mole) prepared as described in part I. The lithium reagent was then added directly to an ether solution of 2-bromo-2-(chlorodimethylsilyl)propane. The work-up of the reaction mixture was identical to that of the previous preparation. Distillation was also done on the annular teflon spinning band column and pure compound was collected at 94°/10mm Hg. (Found: C, 53.30; H, 7.21% mol. wt., 272. Calcd. for $C_{12}H_{19}SiBr$: C, 53.13; H, 7.07% mol. wt., 271.3). The yield of pure product was 64%. The NMR and mass spectral data were recorded.

NMR Data:	Singlet	δ 0.45 (6H)
	Singlet	δ 1.59 (6H)
	Singlet	δ 2.23 (3H)
	Quartet	δ 7.25 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	149	100
	272	< 1

2-Bromo-2-(p-chlorophenyldimethylsilyl)propane

p-Chlorophenyllithium was prepared by adding an ethereal solution of p-bromochlorobenzene (21 g, 0.11 mole) to a cold ether

solution (-10°) of n-butyllithium (0.11 mole) contained in a 500 ml three-neck flask equipped in the usual manner. The cold lithium reagent was added immediately to an ether solution of 2-bromo-2-(dimethylchlorosilyl)propane (0.11 mole) and stirring was continued for 2 hours. The work-up followed the usual pattern with the final distillation being done through a three inch beaded column. Pure product was collected at 69.5-71.0°/0.05mm Hg. (Found: C, 45.25; H, 5.54% mol. wt., 292. Calcd. for $C_{11}H_{16}SiBrCl$: C, 45.29; H, 5.53% mol. wt., 291.7). The yield of pure product was 58%. The NMR and mass spectral data were recorded.

NMR Data:	Singlet	δ 0.45 (6H)
	Singlet	δ 1.65 (6H)
	Quartet	δ 7.39 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	168	100
	292	< 1

2-Bromo-2-(p-anisyldimethylsilyl)propane

p-Anisyllithium was prepared in the usual manner by adding an ether solution of p-bromoanisole (22.4 g, 0.10 mole) to a rapidly stirred ethereal solution of n-butyllithium (0.10 mole) contained in a 500 ml reaction flask equipped in the usual manner. The p-anisyllithium was then added quite rapidly (350 ml in 15 minutes) to an ether solution of 2-bromo-2-(dimethylchlorosilyl)propane contained

in a 500 ml reaction flask equipped in the usual manner. The work-up of the reaction mixture followed the same pattern as before and the final distillation was carried out through a three inch beaded column. Pure product was collected at 85°/0.1mm Hg. (Found: C, 49.79; H, 6.65% mol. wt., 288. Calcd. for $C_{12}H_{19}SiBrO$: C, 50.17; H, 6.66% mol. wt., 287.3). The yield of pure product was 51%. The NMR and Mass Spectral Data were recorded.

NMR Data:	Singlet	δ 0.42 (6H)
	Singlet	δ 1.63 (6H)
	Singlet	δ 3.72 (3H)
	Quartet	δ 7.12 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	108	100
	137	22
	165	65
	288	< 1

2-Bromo-2-(p-fluorophenyldimethylsilyl)propane

p-Fluorophenyllithium was prepared by adding p-bromofluorobenzene (9.8 g, 0.056 mole) to an ethereal solution of n-butyllithium at -10° and added immediately to the chlorosilane. Stirring was continued for one hour after the addition of the lithium reagent was complete, and the work-up of the reaction mixture followed the usual pattern. The product was distilled through a three inch

beaded column and collected at 57°-58°/0.1mm Hg. (Found: C, 47.94; H, 5.94% mol. wt., 276. Calcd. for $C_{11}H_{16}SiBrF$: C, 48.00; H, 5.86% mol. wt., 275.3). The NMR spectrum was recorded.

NMR Data:	Singlet	δ 0.45 (6H)
	Singlet	δ 1.68 (6H)
	Sextet	δ 7.30 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	153	100
	276	< 1

2-Bromo-2-(m-tolyldimethylsilyl)propane

m-Tolyllithium was prepared by adding an ether solution of m-bromotoluene (9.6 g, 0.056 mole) to an ethereal solution of n-butyllithium (0.056 mole) cooled to -30° and contained in a 500 ml reaction flask equipped in the usual manner. After the addition of the m-bromotoluene was complete, the lithium reagent was stirred for 30 minutes and transferred immediately to a 500 ml cold-finger addition funnel. The low temperature was maintained throughout the addition of the lithium reagent to the 2-bromo-2-(dimethylchlorosilyl)propane (0.056 mole). The work-up of the reaction mixture followed the usual pattern and distillation through a three inch beaded column produced pure product boiling at 60°-61°/0.1mm Hg. Found: C, 53.39; H, 7.24% mol. wt., 272. Calcd. for $C_{12}H_{19}SiBr$: C, 53.13; H, 7.06% mol. wt., 271.3). The yield of pure product was 51.5%. The NMR spectrum was recorded.

NMR Data:	Singlet	δ 0.45 (6H)
	Singlet	δ 1.68 (6H)
	Multiplet	δ 7.18-7.59 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	149	100
	272	< 1

2-Bromo-2-(p-bromophenyldimethylsilyl)propane

2-Bromo-2-(p-bromophenyldimethylsilyl)propane was prepared in a manner exactly analogous to the previous compound except that the 2-bromo-2-(dimethylchlorosilyl)propane was also kept at -30° during the entire addition of the lithium reagent. After the addition was complete, the mixture was stirred until room temperature was attained. Distillation was carried out as before and pure product was collected at 96-97°/0.2mm Hg. (Found: C, 39.20; H, 4.79% mol. wt., 337. Calcd. for $C_{11}H_{18}SiBr_2$: C, 39.30; H, 4.79% mol. wt., 336.1). After approximately one week in a glove bag under nitrogen, the compound crystallized, m.p. 45-46° in a sealed tube. The yield of pure product was 8 g (24%). The NMR spectrum was recorded.

NMR Data:	Singlet	δ 0.52 (6H)
	Singlet	δ 1.68 (6H)
	Singlet	δ 7.40 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	213	100
	337	< 1

2-Bromo-2-(m-chlorophenyldimethylsilyl)propane

2-Bromo-2-(m-chlorodimethylsilyl)propane was prepared in a manner exactly analogous to the preceeding preparation. The final distillation was also through a three inch beaded column and pure product was collected at 79-80°/0.15mm Hg. (Found: C, 45.19; H, 5.57%, mol. wt., 291. Calcd. for $C_{11}H_{16}SiBrCl$: C, 45.29; H, 5.53%, mol. wt., 291.7). The yield was 40%.

NMR Data:	Singlet	δ 0.45 (6H)
	Singlet	δ 1.68 (6H)
	Multiplet	δ 7.18-7.59 (4H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	169	100
	291	< 1

Solvolysis Reactions

Materials. The 2-bromo-2-(aryldimethylsilyl)propane substrates were purified by distillation and accepted as pure on the basis of boiling point range, NMR spectra, C-H analysis, mass spectral data, and thin layer chromatography. The aqueous ethanol solvent was prepared as previously described and the absolute ethanol was used

without further purification. The approximately 0.01M sodium hydroxide was the same as used before.

Kinetic Measurements. Kinetic measurements were carried out as previously described except that the silyl halide being reacted was first dissolved in 5 ml of absolute ethanol and then added to 200 ml of the aqueous ethanol solvent. This mixture (approximately 0.015M in silane) was then pipetted into the 5 ml ampoules and the same procedure followed as before.

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CHAPTER III

The aluminum chloride catalyzed rearrangement of triorgano-(chloromethyl)silanes has been rather extensively studied[1,2] The general reaction scheme is pictured in Reaction 1-7. Originally, Whitmore, Sommer, and Gold[1] proposed that the mechanism of this rearrangement was analogous to the well-known Wagner-Meerwein rearrangement (Reaction 3-1).

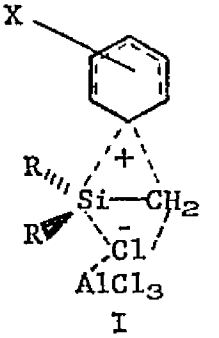
Reaction 3-1

$$Me_3SiCH_2Cl + AlCl_3 \rightarrow Me_3SiCH_2^+ + AlCl_4^-$$

$$Me_2\overset{Me}{\overset{|}{Si}}CH_2^+ \rightarrow Me_2\overset{+}{Si}CH_2CH_3$$

$$Me_2\overset{+}{Si}CH_2CH_3 + AlCl_4^- \rightarrow Me_2\overset{Cl}{\overset{|}{Si}}CH_2CH_3 + AlCl_3$$

Later, Bott, Eaborn, and Ruston[3] made a systematic study of the migratory aptitudes of substituted phenyl groups in the analogous $AlCl_3$ catalyzed rearrangement of $X\text{-}C_6H_4(CH_3)_2SiCH_2Cl$. The data which they obtained led them to favor a mechanism involving a four-center transition state (I) rather than a carbonium or siliconium ion intermediate.

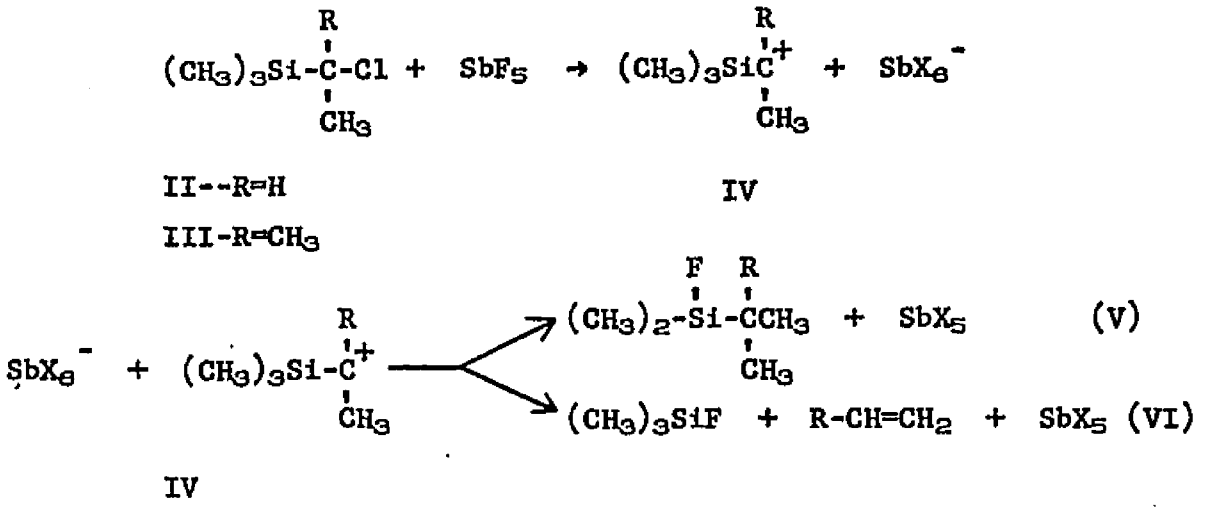


I

Their data also revealed that the relative migratory aptitudes of the variously substituted phenyl groups was dependent on the electron releasing ability of the phenyl substituent (migratory aptitude: p-Me > H > p-Cl). In a later study by Steward, Uhl, and Sands[4] of the relative migratory aptitude of various alkyl groups in the same $AlCl_3$ catalyzed rearrangement reaction, two apparent trends were found: (1) the positive inductive effect of the alkyl moieties facilitates migration from silicon to carbon, and (2) branching at the α-carbon inhibits migration of the branched alkyl group relative to methyl (migratory aptitude: n-propyl > ethyl > methyl > isopropyl). The relative migratory aptitudes also led the authors to conclude that the mechanism of this reaction involved a four-center transition state with synchronous intramolecular migration of the organic group and the chloride ion.

Since the previous work of Eaborn and others involved only catalytic amounts of $AlCl_3$, the order of the rearrangement reaction with respect to Lewis acid could not be determined even though Eaborn[3] had shown the reaction to be first order with respect to the silyl substrate. To determine the kinetic dependence of the Lewis acid rearrangement with respect to the various species present, Hairston and O'Brien[5] prepared II and III and reacted these two compounds in the presence of the Lewis acid, SbF_5, dissolved in nitromethane (Reaction 3-2).

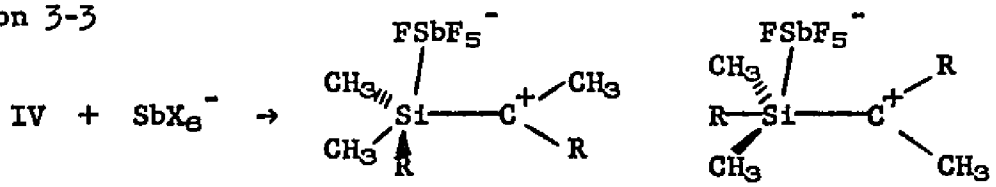
Reaction 3-2



For III the initial ionization is a second order reaction, first order in both III and SbF_5. The intermediate IV (observed by NMR) then reacts in a consecutive second-order manner to yield V (90%) and VI. For the secondary halide, II, the initial ionization becomes the rate determining step and the only reaction observed by NMR is the disappearance, due to β-elimination, of resonances due to methyl and methylene protons. The extent of elimination for II was greater than 98% as determined by NMR. However, it was shown that the rate constant for II was dependent on the concentration of SbF_5. O'Brien concludes that the species IV is best described as a donor-acceptor complex rather than a free carbonium ion since the chemical shifts of the starting silane NMR resonances were only slightly shifted downfield in IV relative to starting material. Since the rate of disappearance of IV shows first-order dependence on the concentration of the hexahaloantimonate ion, O'Brien expresses the opinion that the

reaction 3-2 is best described by the attack of the hexahaloantimonate ion at silicon either before or during the rate determining step of alkyl migration, i.e., a pentacovalent silicon intermediate (Reaction 3-3). O'Brien also found that the amount of rearranged product obtained was dependent of the size of the migrating group, a fact which had been previously observed by others.[4,6] In a transition state such as VII or VIII a large bulky group, e.g. t-butyl or

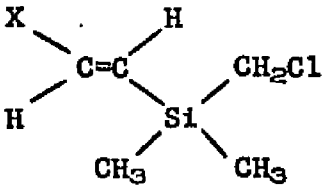
Reaction 3-3



VII VIII

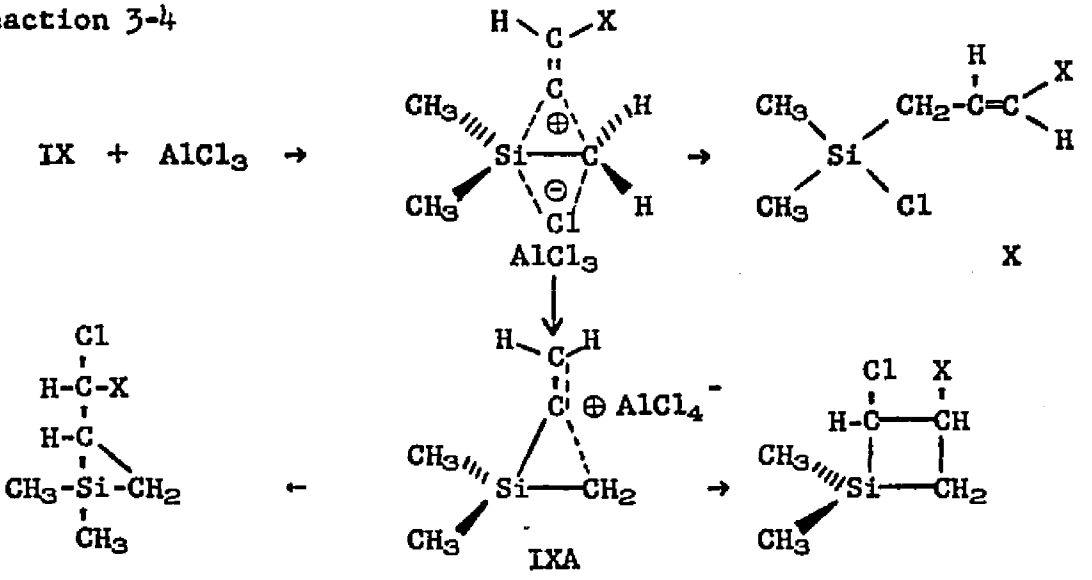
isopropyl, would be expected to be in the apical position, VIII, and migration from this position to the likewise apical cationic center would be severely inhibited. Experimentally, it is observed that t-butyl and isopropyl groups fail to migrate. A pentacovalent silicon intermediate offers an interesting alternative view to the four-center transition state proposed by Eaborn. It should be noted that no evidence is offered by O'Brien which eliminates the possibility of the existence of a four-center intermediate and, in fact, one might propose a four-center intermediate involving pentacoordinate silicon with flank attack by the SbF_6^- being assured by prior coordination with the cationic center.

Notably missing from any reports on the Lewis-acid catalyzed rearrangements of organosilanes is the migrating ability of vinyl groups. In a compound such as IX the vinyl group might be expected to migrate in preference to a methyl group. This particular rearrangement would be of interest because of the possibility of trapping small ring compounds (Reaction 3-4).



IX

Reaction 3-4



The homoallylic ion (IXA) represents a structure quite commonly proposed in the analogous all-carbon system (XI).

XI

It has been shown experimentally that considerable stability can be attained by carbonium ions when a vinyl group is attached to the β-carbon atom which can interact with the positive center on the α-carbon.[7]

If the homoallyic ion IX-A does exist for the silicon system, a substituent, X, which could stabilize a carbonium ion, i.e., a phenyl group, might enhance the probability of trapping the silacyclopropane. With this in mind Reaction 3-4 was then carried out under various conditions (Table 3-1). In no case was the expected rearrangement

Table 3-1[a]

run number	Compound IX	mole ratio Silane/$AlCl_3$	temperature	products and comments
1	X=H	4/5	25°	Me_2SiCl_2, polymer
2	X=H	1/1	25°	Me_2SiCl_2, polymer
3	X=H	5/7	0°	Me_2SiCl_2, polymer
4	X=H	6/5	-20°	no reaction after 12 hrs.
5[b]	X=H	7¼/1	-10 to 25°	Me_2SiCl_2, polymer
6	X=phenyl	1/1	25°	Me_2SiCl_2, polymer

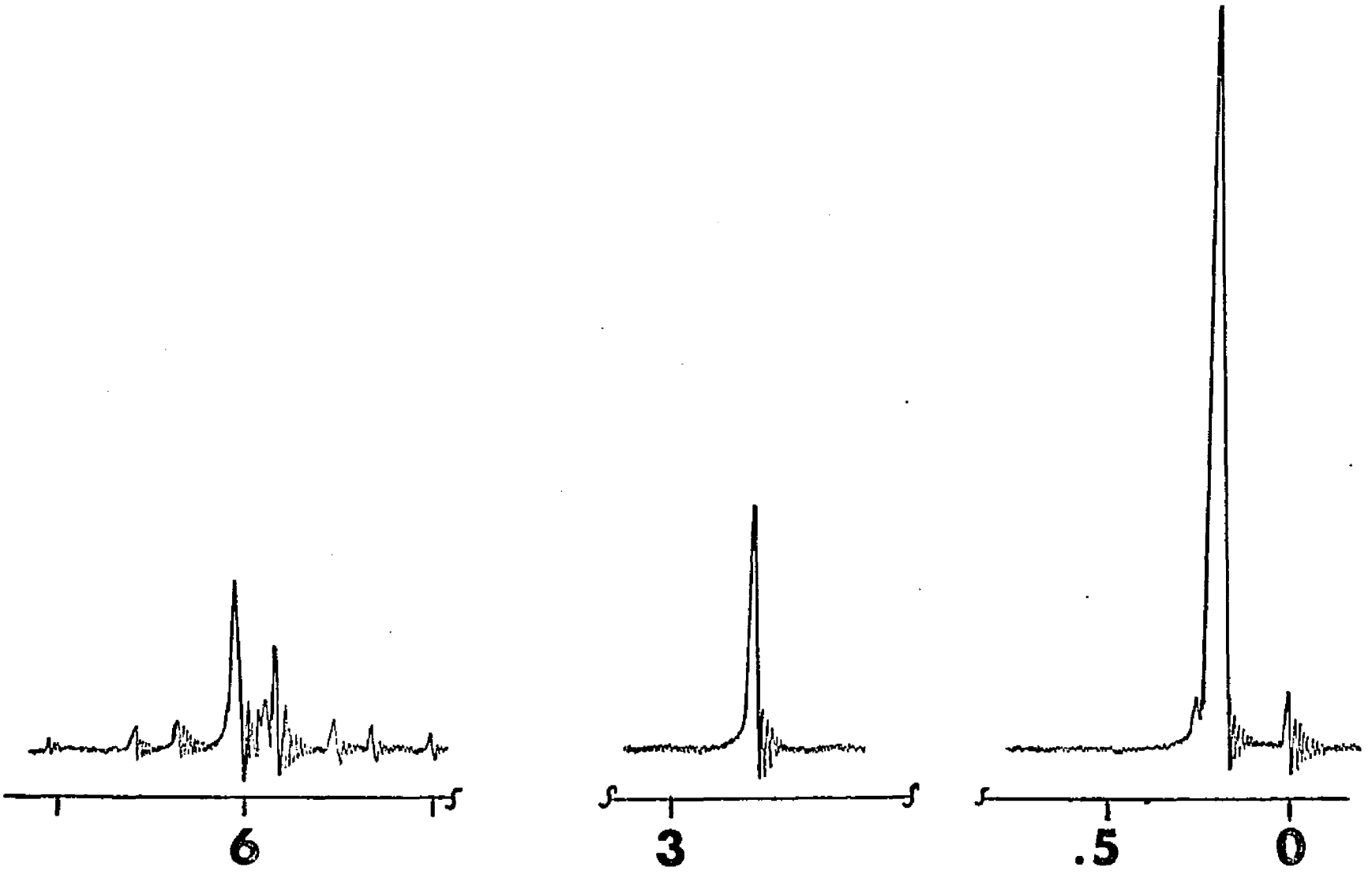
[a]The solvent in each case was Me_2Cl_2 unless otherwise noted.
[b]Neat

product, X, isolated nor were any small ring compounds observed by NMR (see spectra 3-1 and 3-2). The fact that dichlorodimethylsilane is observed in each case and that the vinyl and methylene protons disappear indicates that cleavage and polymerization reactions predominate. Since vinylsilane polymerization does not occur readily and ethylene was not evolved, it is possible that rearrangement occurs prior to cleavage to yield an allylsilane which is known to polymerize in the presence of $AlCl_3$ to yield polymeric material of low molecular weight.[8] It is interesting that no methyl migration is observed. The homoallylic structure, IX-A, may lower the transition state energy for vinyl migration relative to the methyl migration allowing the vinyl group to migrate to the exclusion of methyl. This would be similar to phenyl migration which occurs some 700 times faster than methyl migration.[4]

There were other attempts made to induce vinyl migration in IX by producing a cationic center adjacent to silicon. IX (X=H) was reacted in excess trifluoroacetic acid at 70° for 18 hours. The NMR spectrum of the reaction mixture revealed that the vinyl group had completely reacted. Work-up and distillation of the reaction mixture yielded about 4 ml of compound boiling at 53-60°/0.5mm Hg. An infrared spectrum of this latter compound revealed the presence of an Si-O linkage and the NMR spectrum showed two sets of non-equivalent protons 0.20 δ (singlet) and 2.75 δ (singlet). The IR and NMR data are consistent with the structure XII. This product is presumably being formed by the following route:

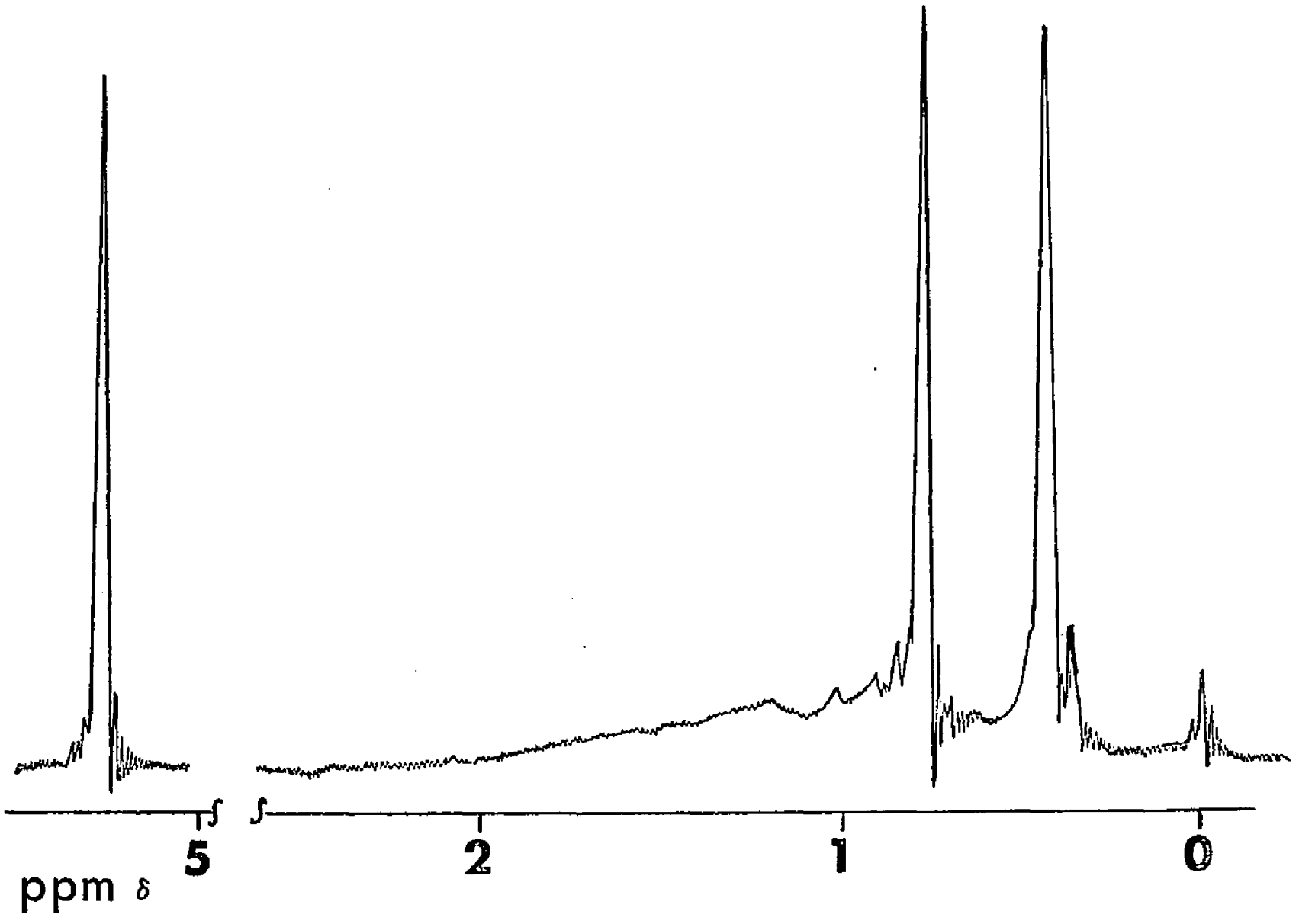
Spectrum 3-1

60 MHz ^{1}H-NMR Spectrum of Chloromethyldimethylvinylsilane in Carbon Tetrachloride

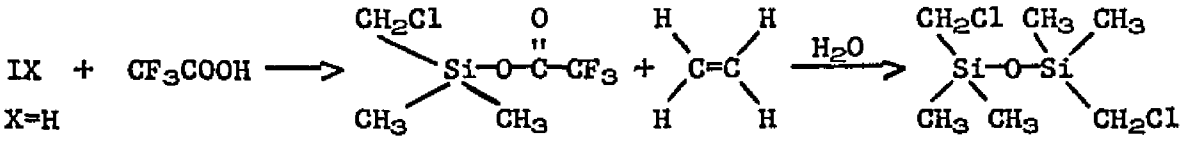

6
3
.5
0
ppm δ

Spectrum 3-2

60 MHz ^{1}H-NMR Spectrum of the Reaction Mixture after the Addition of $AlCl_3$ to Chloromethyldimethylvinylsilane in Methylene Chloride Solvent (Run 2, Table 3-1)


5
2
1
0
ppm δ

Reaction 3-5



XII

It is quite probable that the Reaction 3-5 is occurring since it is not uncommon for acids to cleave vinyl groups from silicon,[8,9] and hydrolysis of acyloxysilanes to form disiloxanes is well known.[10]

CHAPTER III

Experimental

General

See Chapter II.

Vinyl Bromide

Vinyl bromide was prepared by dropping 1,2-dibromoethane (175 ml, 2.01 moles) into an excess solution (1000 ml) of 20% potassium hydroxide in 95% ethanol. The mixture was contained in a 2000 ml three-neck flask equipped in the usual manner except that in place of the reflux condenser was connected a dry ice-acetone cold trap. The vinyl bromide which condensed in the trap was washed with water at 0°, dried over $CaCl_2$, and used without further purification. Yield was 79.0 g, 37%.

Chloromethyldimethylvinylsilane

In a 2000 ml three-neck flask was placed 22.6 g (0.93 g atom) of magnesium turnings, and enough THF was added to cover the magnesium. The vinyl bromide was placed in the addition funnel and diluted with 100 ml of THF. This solution was added to the magnesium at such a rate as to maintain a gentle reflux. As soon as the reaction was initiated, an additional 300 ml of THF was added to the magnesium.

Chloromethyldimethylchlorosilane (35.5 g, 0.25 mole) was placed in a 500 ml three-neck flask equipped in the usual manner and diluted with 50 ml THF. An equimolar amount of the vinyl magnesium bromide (determined by titration) was placed in the dropping funnel

and allowed to drip into the rapidly stirred solution of chlorosilane at the rate of about 1 drop per second. After the addition was complete the mixture was stirred for two hours and then added to a saturated aqueous ammonium chloride solution. The THF layer was placed over calcium chloride and allowed to stand overnight. Distillation of the whole THF mixture through a six inch Vigreaux column yielded 13.5 g (45% yield) of chloromethyldimethylvinylsilane, b.p. 120-121°/760mm Hg. (Literature: 119-120°/760mm Hg).[11] The NMR and Mass Spectral data were recorded.

NMR Data:	Singlet	δ 0.21 (6H)
	Singlet	δ 2.76 (2H)
	Multiplet	δ 5.50-6.31 (3H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	85	100
	134	not observed

β-(chloromethyldimethylsilyl)styrene

The same procedure was followed as above. The β-bromostyrene was vacuum distilled and used immediately to make the Grignard reagent. Yield of the silylstyrene was 12 g (26%), b.p. 63-67°/0.5mm Hg; $n_D^{25^\circ}$ = 1.5517. The NMR and Mass Spectral data were recorded.

NMR Data:	Singlet	δ 0.29 (6H)
	Singlet	δ 0.82 (2H)
	Quartet	δ 6.68 (2H)
	Multiplet	δ 7.15-7.49 (5H)

Mass Spectral Data:	m/e	Relative Abundance (70 ev)
	161	100
	145	30
	210	10

Attempted Rearrangement of Chloromethyldimethylvinylsilane

In a typical experiment (run 1, Table 3-1) $AlCl_3$ (6.7 g, 0.05 mole) was sublimed directly into a 100 ml single neck flask equipped with a side-arm connected to an argon train. Sublimation of the $AlCl_3$ took place in a small flask connected to the reaction flask by an elbow joint. To the sublimed $AlCl_3$ was added 25 ml of methylene chloride which had been recently distilled over CaH_2. The mixture was stirred for about 30 minutes to dissolve as much $AlCl_3$ as possible. After this time chloromethyldimethylvinylsilane (5.22 g, 0.04 mole) was dissolved in 25 ml of the freshly distilled methylene chloride and added slowly to the $AlCl_3$ via an addition funnel attached to a reflux condenser which had replaced the elbow joint in the reaction flask. The $AlCl_3$-silane mixture immediately turned brown and a considerable amount of heat was evolved as evidenced by refluxing methylene chloride. An NMR spectrum of the reaction mixture revealed the immediate disappearance of the vinyl and chloromethyl groups. The only identifiable

products (NMR) were dichlorodimethylsilane and polymer. Even though the reaction conditions were varied considerably (see Table 3-1) these two latter products seemed to form each time.

Solvolysis of Chloromethyldimethylvinylsilane with Trifluoroacetic Acid

Trifluoroacetic acid (10.6 g, 0.1 mole) was added to chloromethyldimethylvinylsilane (7.2 g, 0.05 mole) contained in a 125 ml single-neck flask equipped with a reflux condenser. The reflux condenser was connected to a nitrogen train. The flask was heated with a heating mantle to 60-70° and left at this temperature for 18 hours. After this time the reaction mixture was placed in a separatory funnel and washed twice with 25 ml portions of ether. The ether layer was washed 8 times with 30 ml portions of water and then placed over $CaCl_2$ to dry. Distillation of the ether layer yielded about 4 ml of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane boiling at 53-60°/0.5mm Hg (Literature b.p. 92°/21mm Hg).[12] The NMR and infrared data were recorded.

NMR Data:	Singlet	δ 0.20
	Singlet	δ 2.75
Infrared Data:	8.5-9.5 cm^{-1} (broad band)	

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CHAPTER III

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APPENDIX

Specific Rate Data

Collected from Chapter II

Table A-1

The Solvolysis of 2-Bromo-2-(trimethylsilyl)propane(I)

in 54 Volume % Aqueous Ethanol at 85.0° ± 0.1°

time, min	ml titrant[a] required for 5 ml aliquot
	run 1 (ca. 0.01M I)[b]
0	1.74
5	2.80
30	6.05
50	7.21
75	8.88
90	9.80
110	9.90
135	10.68
24 hours	12.22

[a] 0.01ON NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-1a

Rate Constant Derived from Table A-1[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	24.2 ± 0.4	0.995

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-1

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-1

(a-x) = (titer at infinite time - titer at time, t)

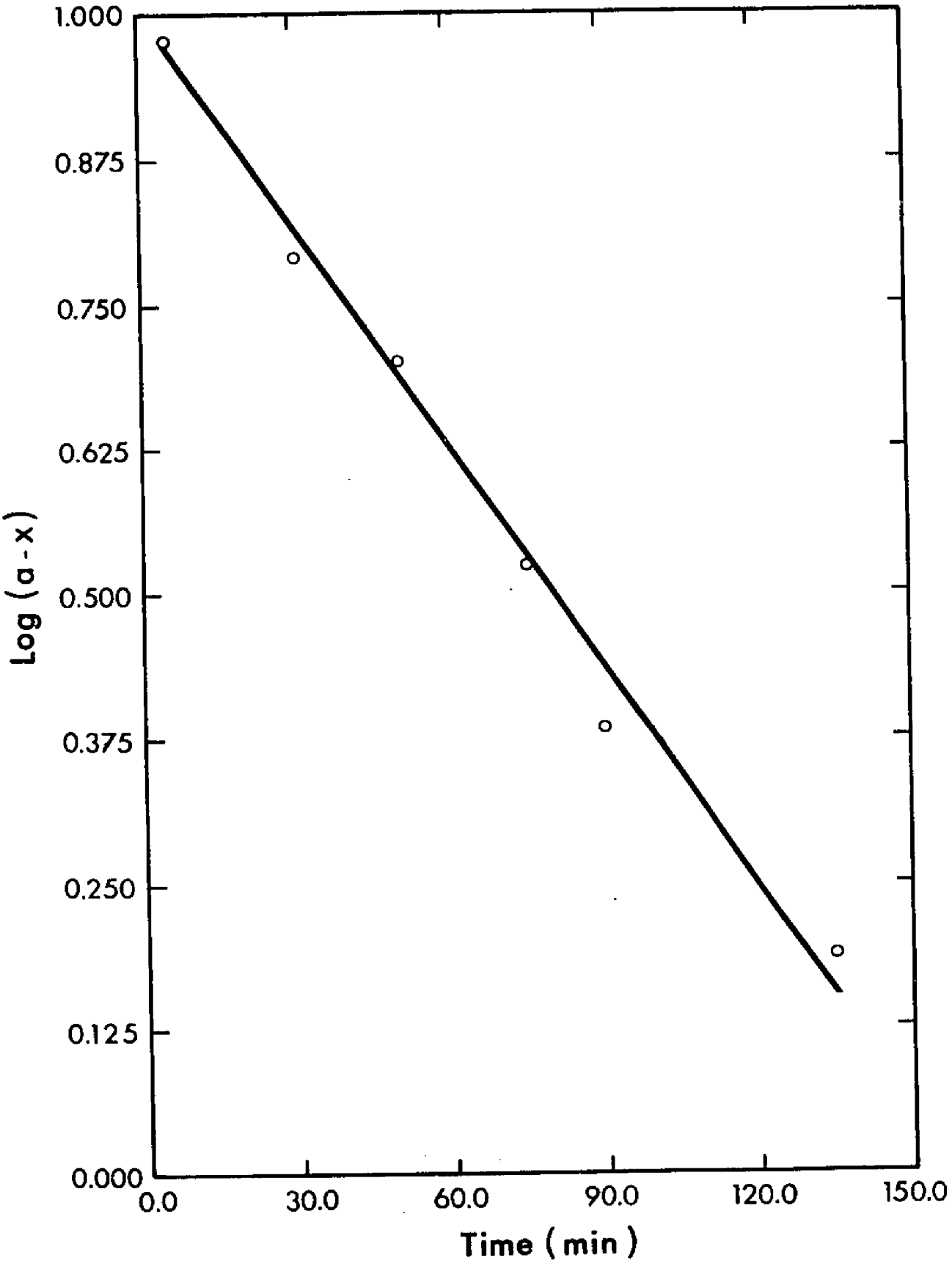

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
30.0
60.0
90.0
120.0
150.0
Time (min)

Table A-2

The Solvolysis of 2-Bromo-2-(trimethylsilyl)propane(I)

in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml of titrant[a] required for 5 ml aliquots	
	run 1 (ca. 0.014M I)[b]	run 2 (ca. 0.014M I)
0	0.30	0.34
20	0.69	0.78
40	1.23	1.14
60	1.65	1.58
80	1.81	1.80
100	2.16	2.22
120	2.52	2.52
140	2.75	2.85
160	2.98	3.00
180	3.20	3.10
2 days	4.60	4.60

[a]0.015M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-2a

Rate Constants Derived from Table A-2[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	10.3 ± 0.1	0.998
2	10.2 ± 0.2	0.996

[a]Error for individual run is the standard deviation from a least square analysis.

Figure A-2

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-2, run 2

(a-x) = (titer at infinite time - titer at time, t)

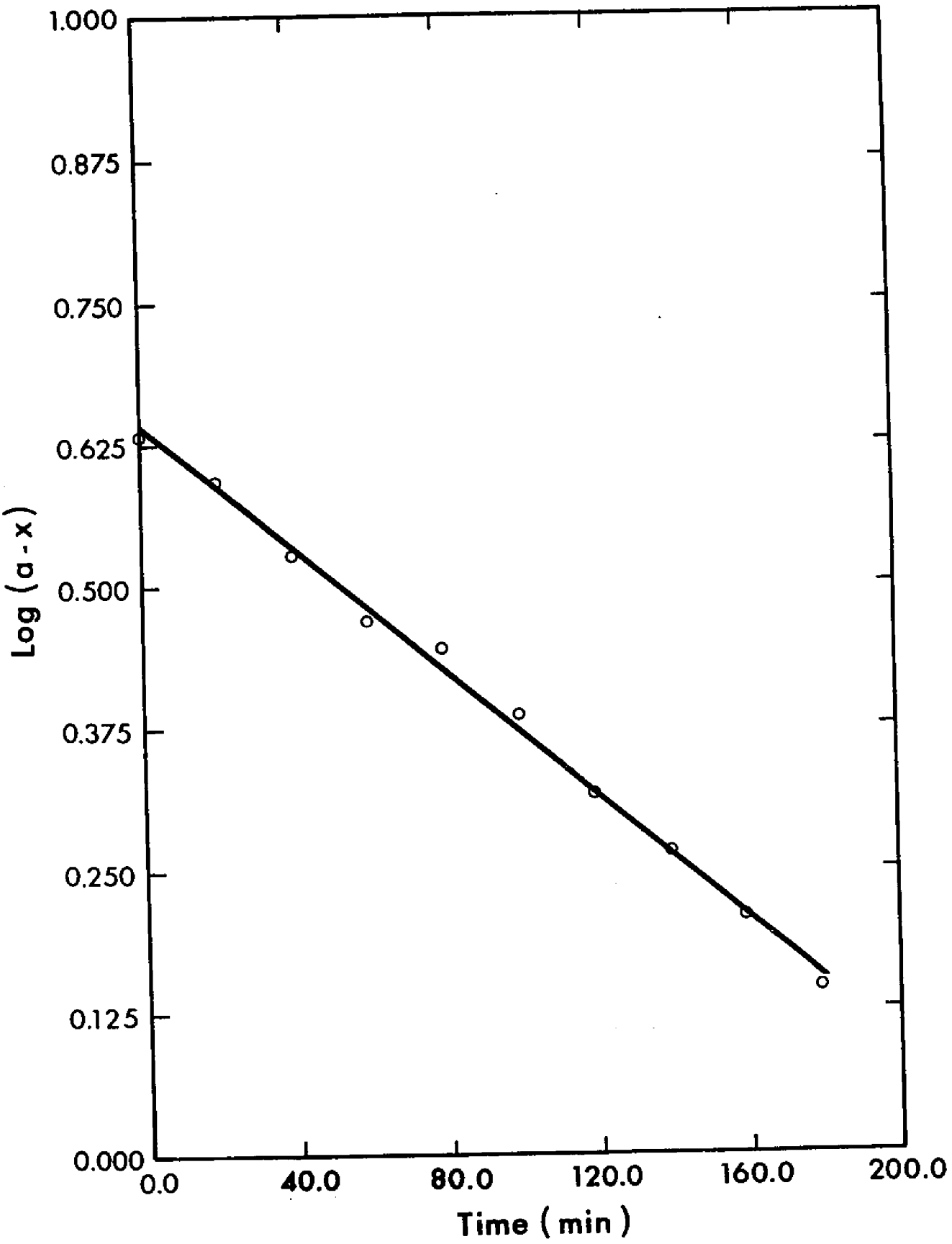

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
40.0
80.0
120.0
160.0
200.0
Time (min)

Table A-3

Solvolysis of 2-Bromo-2-trimethylsilylpropane(I) in

54 Volume % Aqueous Ethanol at 70.0° ± 0.1°

time, hours	ml titrant[a] required for 5 ml aliquots
	run 1[b] (ca. 0.014M I)
0	0.26
1	0.67
2	1.33
3	1.70
5	2.45
7	3.13
8.5	3.53
10.5	3.90
12	4.10
13.5	4.23
3 days	4.85

[a] 0.015M NaOH, Cresol red, indicator.

[b] See experimental section concerning preparation of solution

Table A-3a

Rate Constant Derived from Table A-3[a]

Run	k x 10^5, sec	Correlation Coefficient
1	4.07 ± 0.05	0.997

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-3

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-2

(a-x) = (titer at infinite time - titer at time, t)

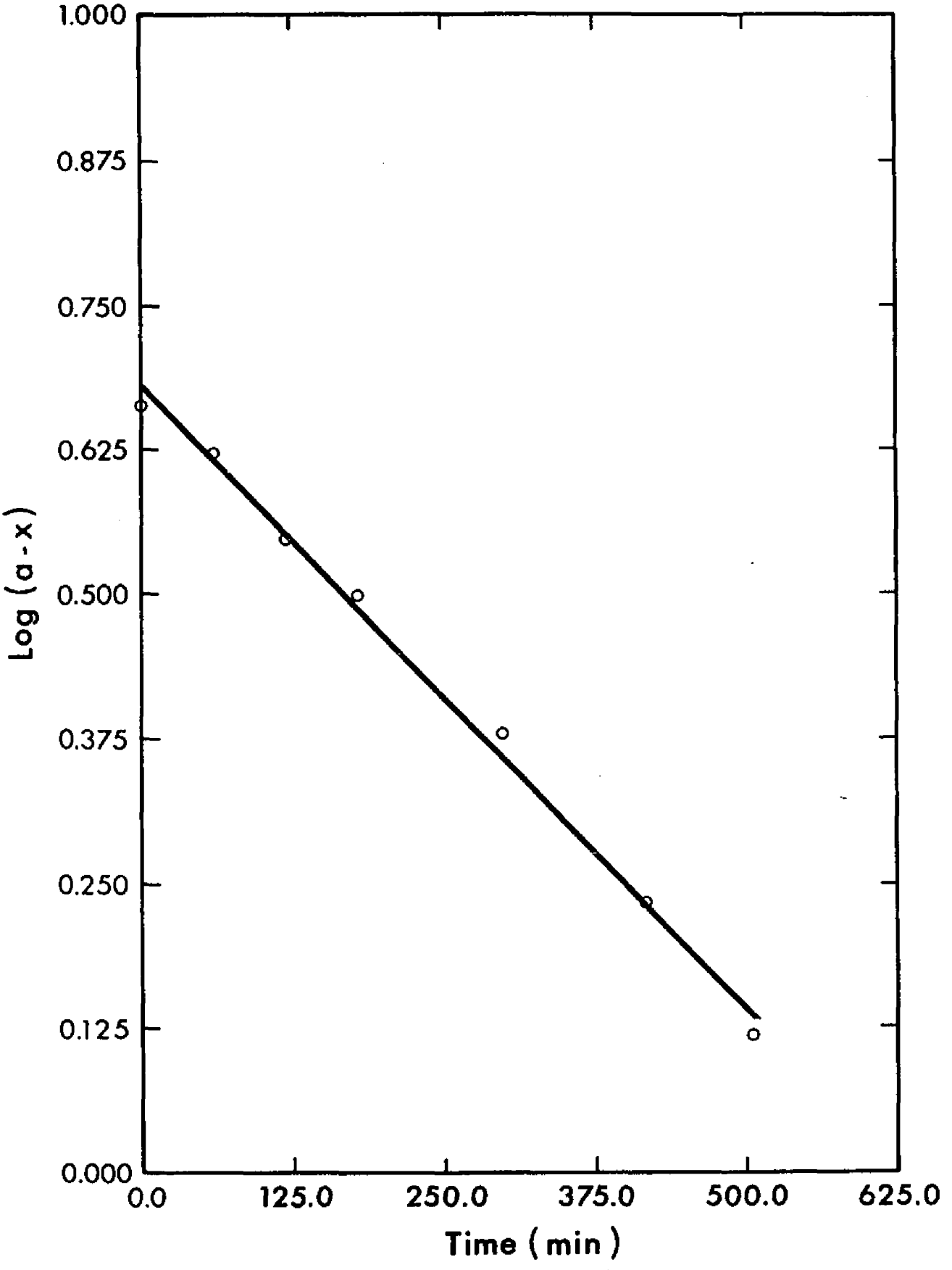

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
125.0
250.0
375.0
500.0
625.0
Time (min)

Table A-4

The Solvolysis 2-Bromo 2-trimethylsilylpropane(I) in 54 Volume % Aqueous Ethanol at $50.0^{\circ} \pm 0.1^{\circ}$

time, hours	ml titrant[a] required for 5 ml aliquots
	run 1 (ca. 0.015M I)[b]
0	0.45
5	0.99
8	1.15
11	1.56
21.5	2.20
27.5	2.62
33.5	2.98
45.5	3.78
51.5	4.03
3 days[c]	7.94

[a] 0.01M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

[c] Three days at 80°.

Table A-4a

Rate Constant Derived from Table A-4[a]

Run	$k \times 10^5$, sec^{-1}	Correlation Coefficient
1	0.349 ± 0.023	0.999

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-4

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-4

(a-x) = (titer at infinite time - titer at time, t)

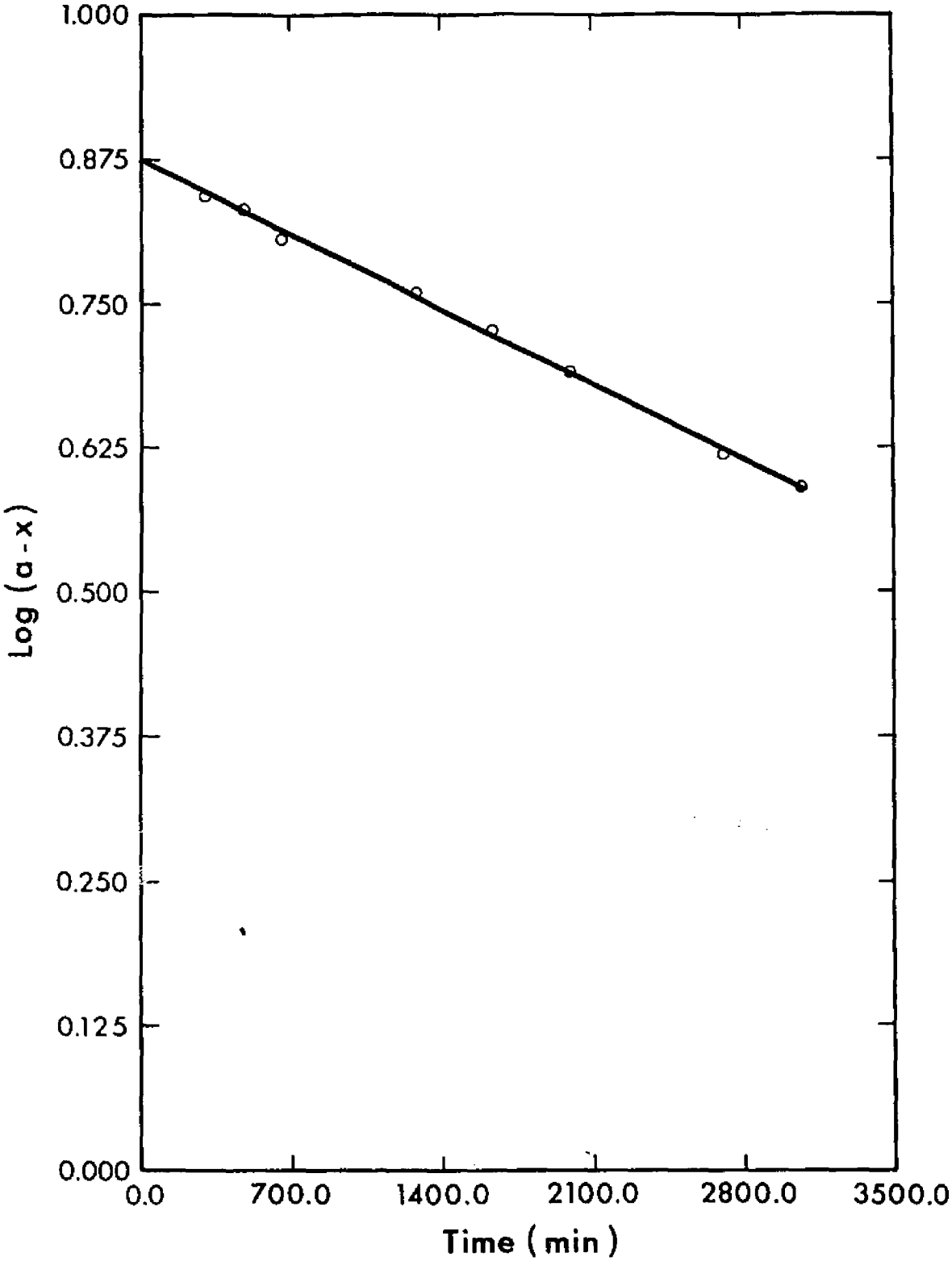

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
700.0
1400.0
2100.0
2800.0
3500.0
Time (min)

Table A-5

The Solvolysis of Dimethyl-t-butylcarbinyl bromide(I)

in 54 Volume % Aqueous Ethanol at 25.0° ± 0.1°

time, min	ml titrant[a] required for 5 ml aliquots	
	run 1 (ca. 0.01M I)[b]	run 2 (ca. 0.01M I)
0	0.90	1.22
0.5	1.40	1.75
1.0	1.80	2.22
1.5	2.10	2.65
2.0	2.50	2.97
2.5	2.82	3.30
3.0	3.03	3.60
3.5	3.17	3.75
4.0	3.70	3.90
4.5	3.56	4.10
45 min	4.13	4.65

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-5a

Rate Constants Derived from Table A-5[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	604 ± 8	0.997
2	649 ± 8	0.998

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-5

Solvolysis of Dimethyl-t-butylcarbinyl Bromide

Data taken from Table A-5, run 1

(a-x) = (titer at infinite time - titer at time, t)

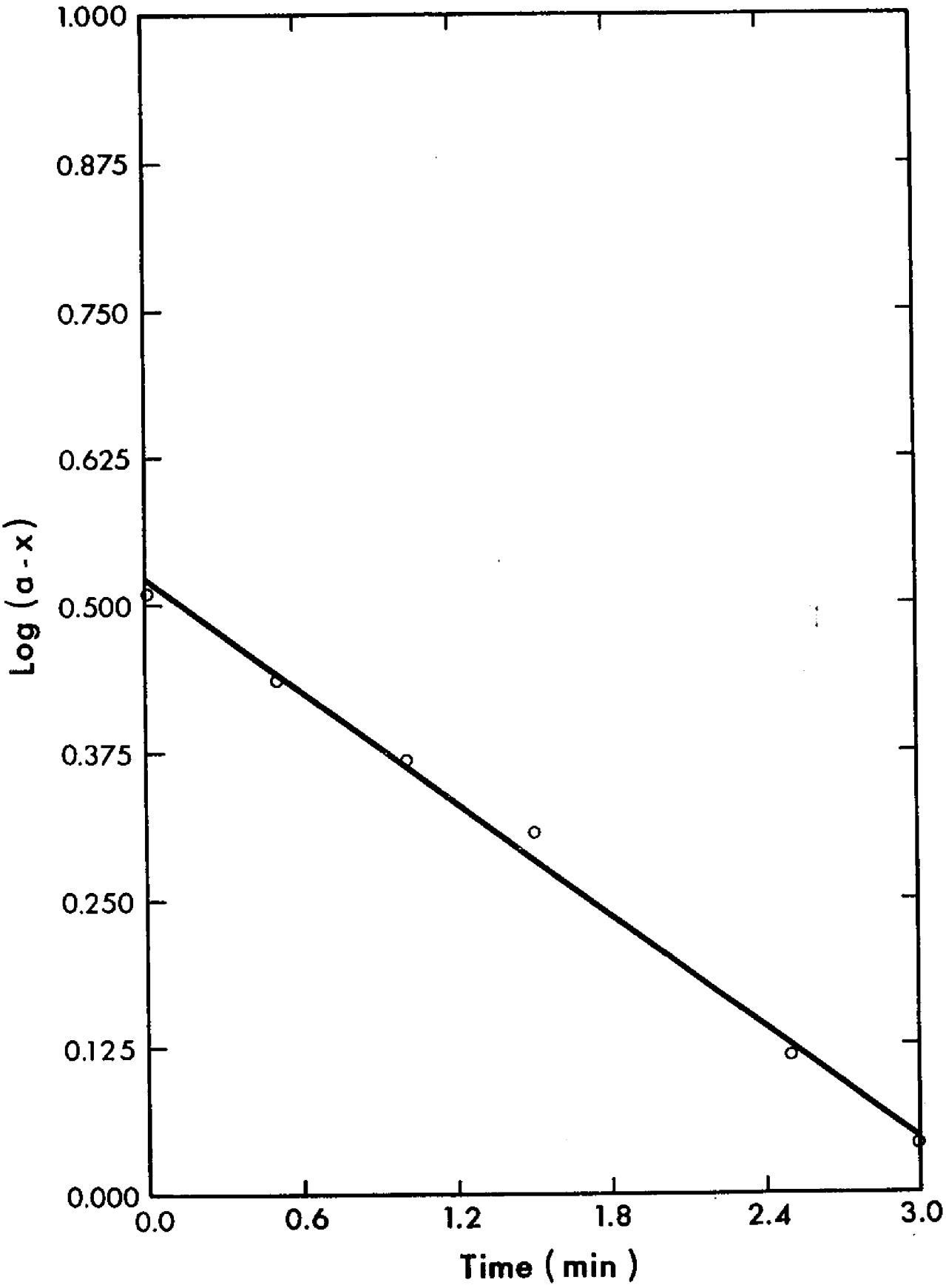

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
0.6
1.2
1.8
2.4
3.0
Time (min)

Table A-6

The Solvolysis of Dimethyl-t-butylcarbinyl Bromide(I)

in 54 Volume % Aqueous Ethanol at 14.8° ± 0.1°

time, min	ml titrant[a] required for 5 ml aliquots
	run 1 (ca. 0.016M I)[b]
1.0	0.80
2.0	1.28
3.0	1.80
4.0	2.35
5.0	2.64
6.0	3.00
7.0	3.36
8.0	3.68
9.0	3.95
10.0	4.20
30 min[c]	6.54

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

[c] Thirty minutes at 25°.

Table A-6a

Rate Constant Derived from Table A-6[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	166 ± 1	0.999

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-6

Solvolysis of Dimethyl-t-butylcarbinyl Bromide

Data taken from Table A-6

(a-x) = (titer at infinite time - titer at time, t)

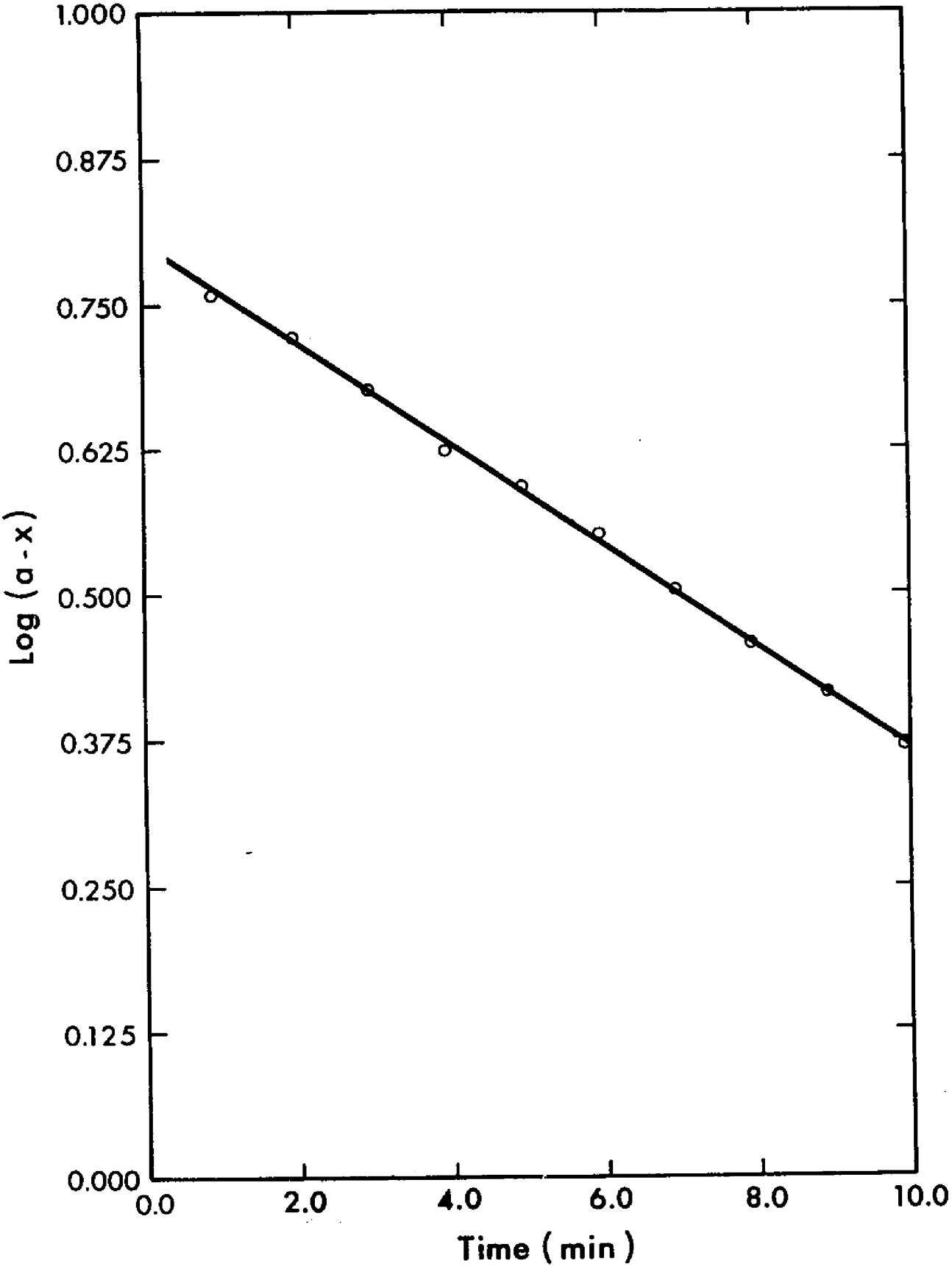

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
2.0
4.0
6.0
8.0
10.0
Time (min)

Table A-7

The Solvolysis of Dimethyl-t-butylcarbinyl bromide

in 54 Volume % Aqueous Ethanol at 2.2° ± 0.2°

time, min	ml titrant[a] required for 5 ml aliquots
	run 1 (ca. 0.010M I)[b]
0	0.42
5	0.66
11	1.02
17	1.30
23	1.65
30	1.95
36	2.15
42	2.30
49	2.60
57	2.76
30 min[c]	4.07

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

[c] Thirty minutes at 25°.

Table A-7a

Rate Constant Derived from Table A-7[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	32.8 ± 0.4	0.997

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-7

Solvolysis of Dimethyl-t-butylcarbinyl Bromide

Data taken from Table A-7

(a-x) = (titer at infinite time - titer at time, t)

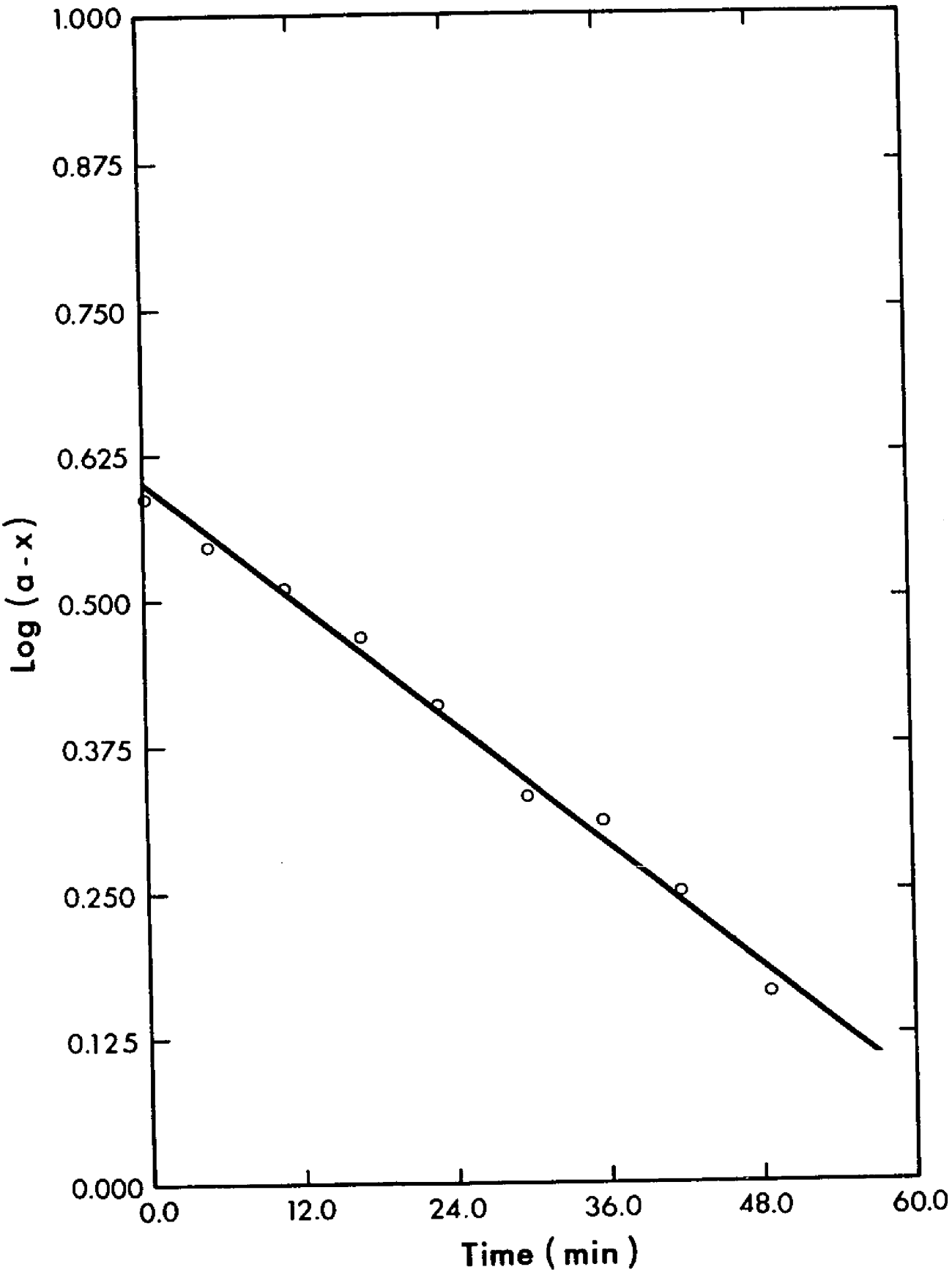

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
12.0
24.0
36.0
48.0
60.0
Time (min)

Table A-8

The Solvolysis of Dimethyl-t-butylcarbinyl Bromide(I)

in 54 Volume % Aqueous Ethanol at -9.2° ± 0.2°

Time	ml of titrant[a] required for 5 ml aliquots
	run 1 (ca. 0.01M I)[b]
0	0.40
15	0.57
30	0.73
60	0.95
90	1.17
120	1.35
150	1.52
180	1.73
210	1.90
30 min[c]	3.91

[a]0.012M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

[c]Thirty minutes at 25°.

Table A-8a

Rate Constant Derived from Table A-8[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	4.29 ± 0.03	0.999

[a]Error for individual run is the standard deviation from a least square analysis.

Figure 8

Solvolysis of Dimethyl-t-butylcarbinyl Bromide

Data taken from Table A-8

(a-x) = (titer at infinite time - titer at time, t)

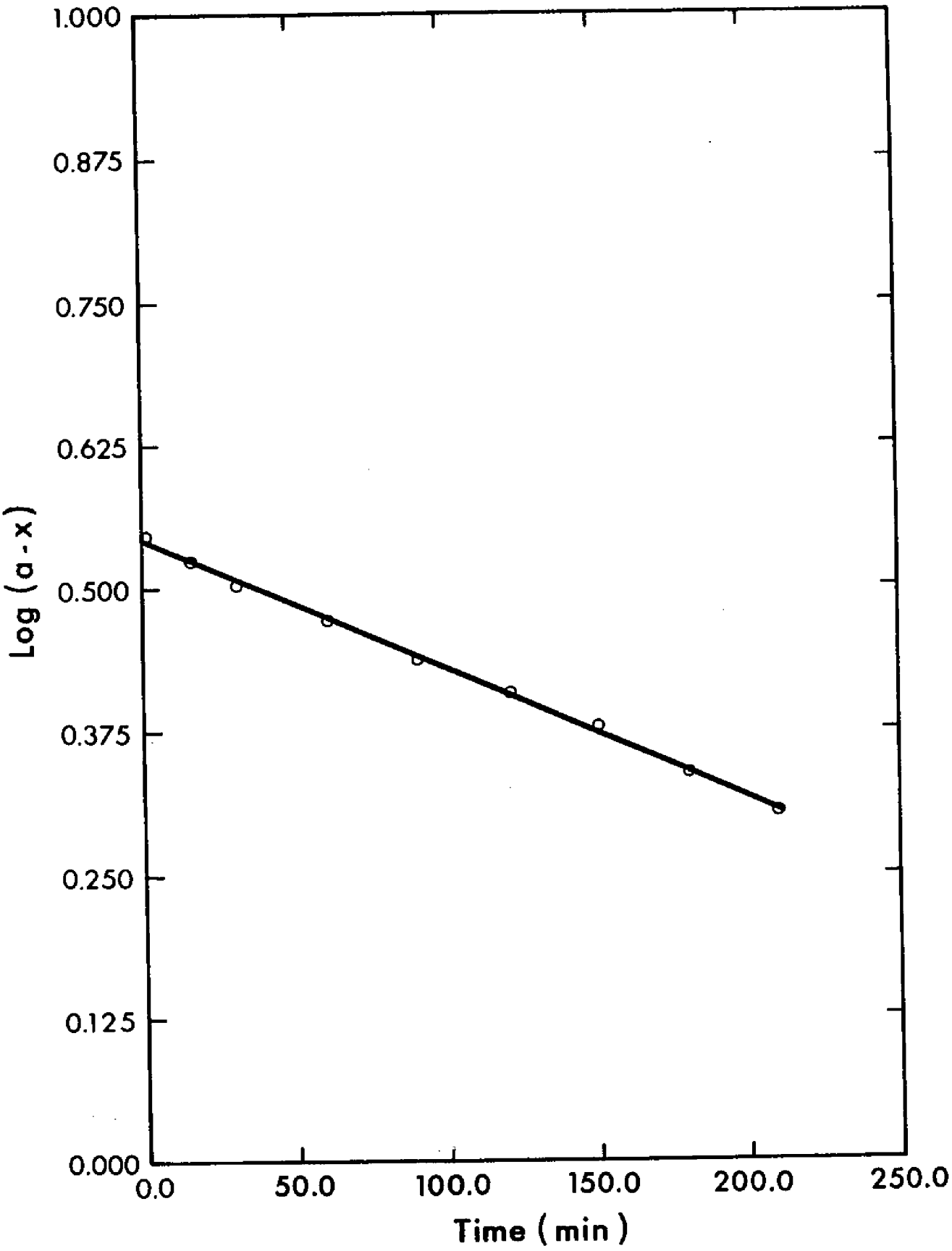

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
50.0
100.0
150.0
200.0
250.0
Time (min)

Table A-9

The Solvolysis of Isopropyl Bromide

in 54 Volume % Aqueous Ethanol at 80° ± 0.1°

time, min	ml titrant[a] required for 5 ml aliquots
	run 1[b] (ca. 0.031N)
0	0.26
15	0.67
45	2.90
75	4.66
105	6.21
135	7.45
165	8.42
190	9.55
205	9.87
48 hours	13.26

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-9a

Rate Constant Derived from Table A-9[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	11.1 ± 0.2	0.996

[a] Error for individual run is the standard deviation from a least square analysis.

Figure 9

Solvolysis of 2-Bromopropane

Data taken from Table A-9

(a-x) = (titer at infinite time - titer at time, t)

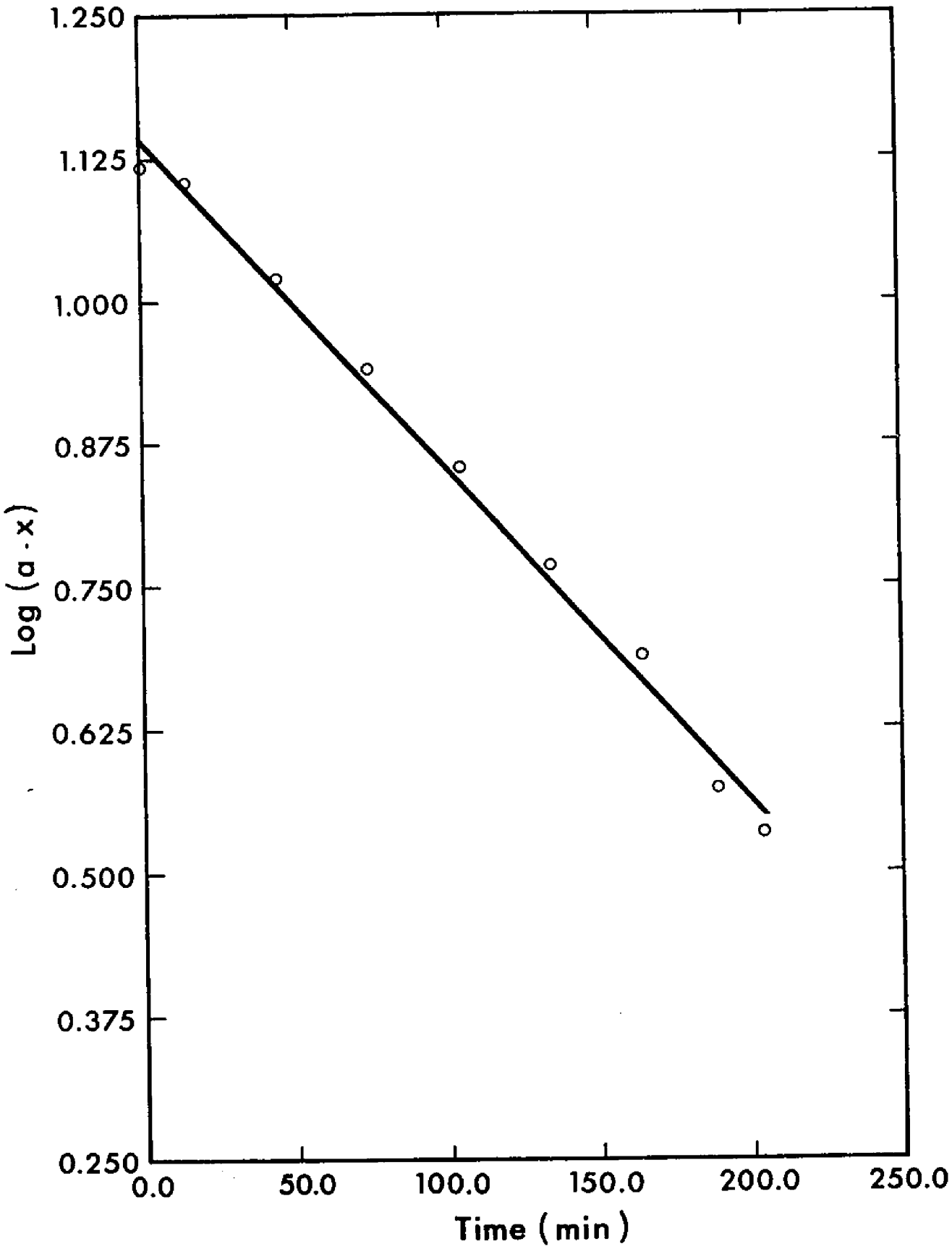

1.250
1.125
1.000
0.875
0.750
0.625
0.500
0.375
0.250
Log (a - x)
0.0
50.0
100.0
150.0
200.0
250.0
Time (min)

Table A-10

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I) in 70 Volume % Aqueous Methanol at 80° ± 0.1° in the presence of LiBr (0.10N)

time,min	ml titrant[a] required for 5 ml aliquots	
	run 1 (ca. 0.019M I)	run 2 (ca. 0.019M I)
0	1.25	1.27
20	1.95	1.95
40	3.15	3.40
60	4.05	4.05
80	4.65	4.70
100	5.17	5.20
120	5.76	5.80
140	6.10	5.95
160	6.40	6.40
48 hours	7.95	7.95

[a]0.012M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-10a

Rate Constants Derived from Table A-10[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	15.7 ± 0.1	0.998
2	15.3 ± 0.2	0.997

[a]Error for individual run is the standard deviation from a least square analysis.

Figure 10

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-10, Run 1

(a-x) = (titer at infinite time - titer at time, t)

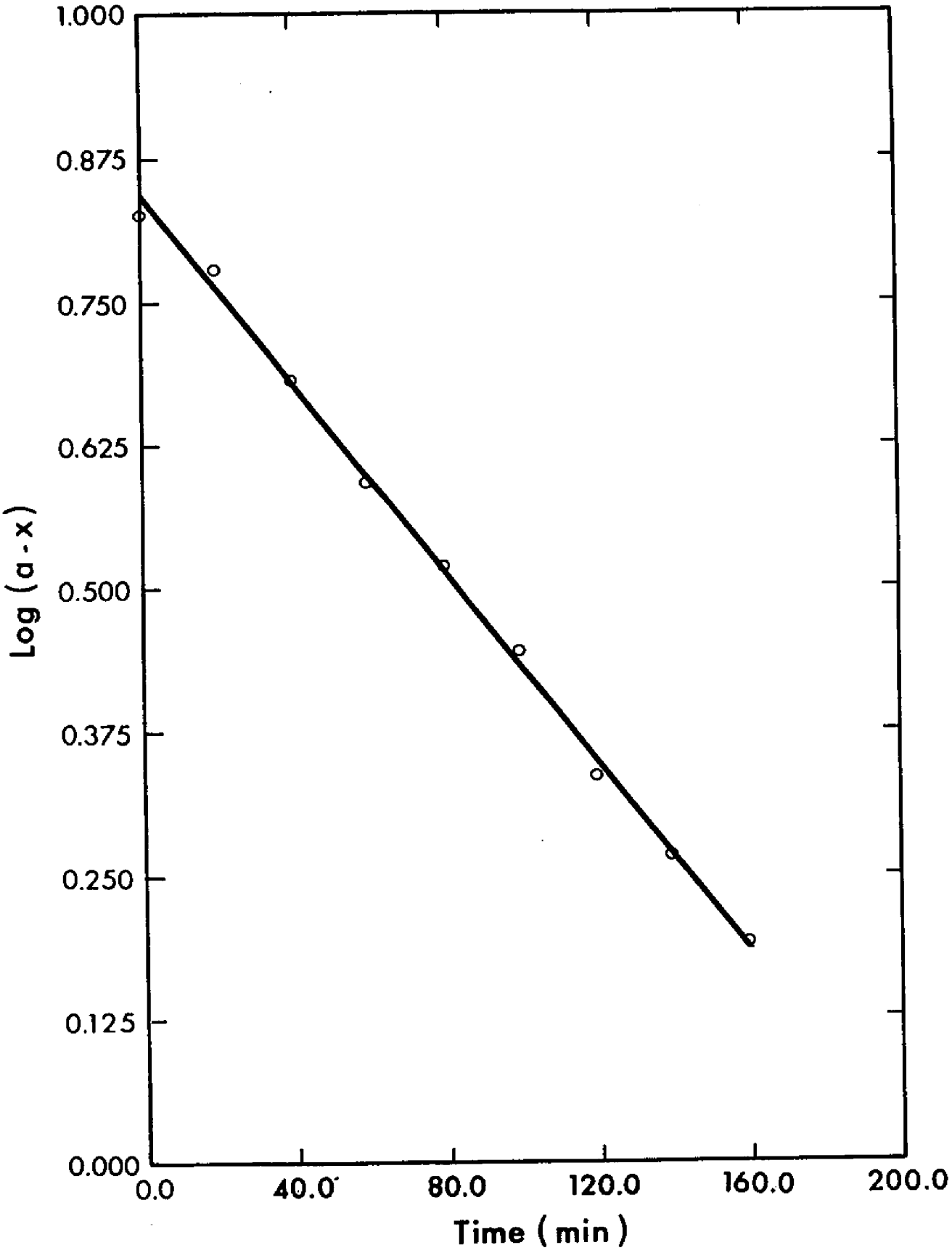

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
40.0
80.0
120.0
160.0
200.0
Time (min)

Table A-11

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1° in the presence of 0.029M NaOH

time,min	ml titrant[a] required for 5 ml aliquots
	run 1 (ca. 0.015M I)[b]
0	9.75
15	9.57
30	8.88
45	8.45
75	7.65
95	7.01
115	6.65
135	6.29
160	6.05
180	5.90
48 hours	4.90

[a] 0.015M HNO_3; cresol red, indicator.

[b] See Experimental section concerning preparation of solution.

Table A-11a

Rate Constant Derived from Table A-11[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	15.6 ± 0.2	0.997

[a] Error for individual run is the standard deviation from a least square analysis.

Figure 11

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-11

(a-x) = (titer at infinite time - titer at time, t)

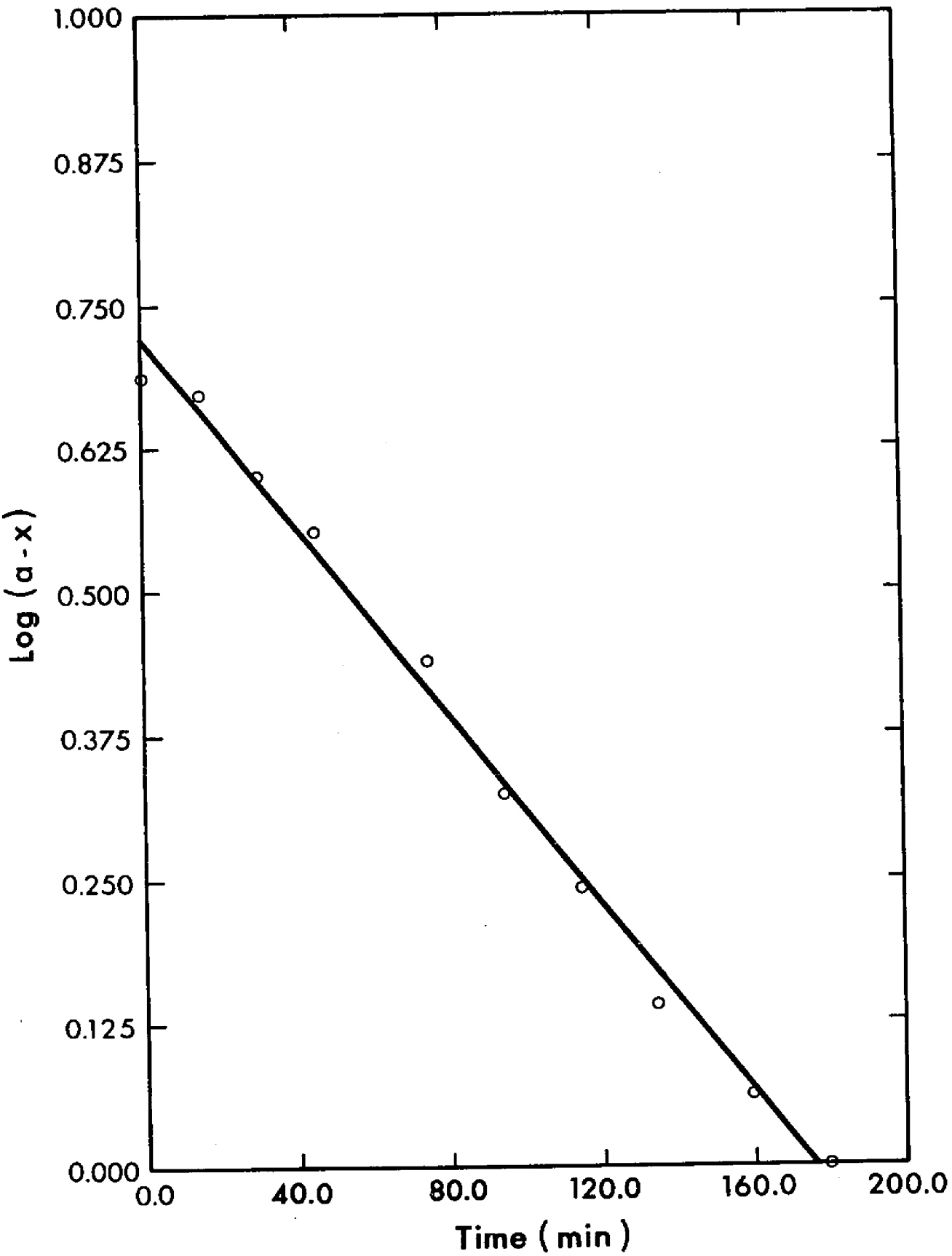

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
40.0
80.0
120.0
160.0
200.0
Time (min)

Table A-12

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 60 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquot
	run 1
	(ca. 0.011M I)[b]
0	0.26
30	0.62
60	1.06
120	1.83
150	2.25
180	2.40
240	2.85
270	3.06
300	3.25
360	3.60
72 hrs	4.80

[a] 0.012M NaOH; Cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-12a

Rate Constant Derived from Table A-12[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	6.33 ± 0.05	0.998

[a] Error for individual run is the standard deviation from a least square analysis.

Figure 12

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-12

(a-x) = (titer at infinite time - titer at time, t)

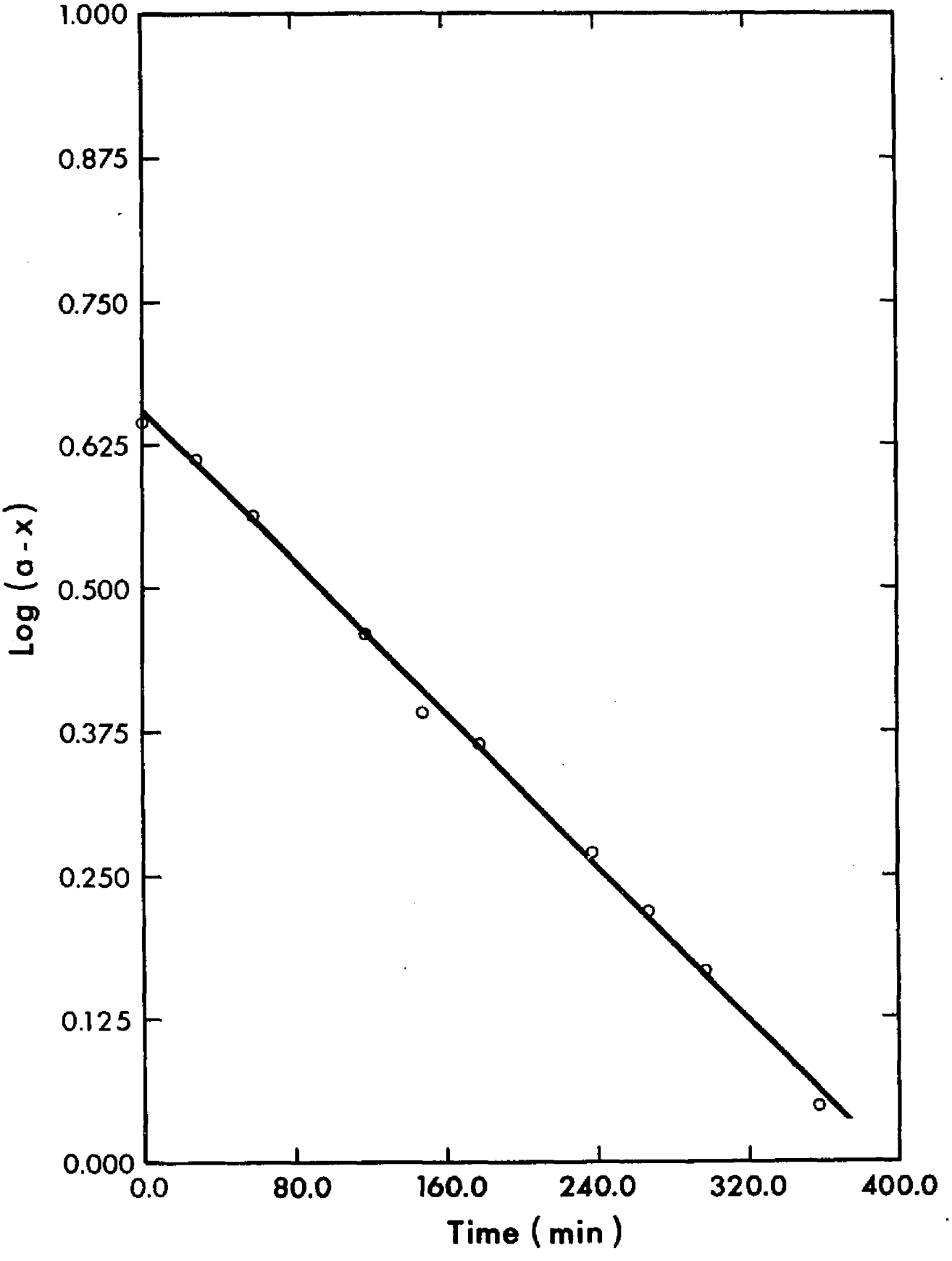

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
80.0
160.0
240.0
320.0
400.0
Time (min)

Table A-13

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 70 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots
	run 1
	(ca. 0.01M I)[b]
0	0.32
60	0.62
120	0.95
180	1.25
240	1.55
300	1.75
390	2.07
540	2.60
630	2.90
750	3.25
4 days	4.39

[a]0.012M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-13a

Rate Constant Derived from Table A-13[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	2.76 ± 0.03	0.997

[a]Error for individual run is the standard deviation from a least square analysis.

Table A-13

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 70 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots
	run 1
	(ca. 0.01M I)[b]
0	0.32
60	0.62
120	0.95
180	1.25
240	1.55
300	1.75
390	2.07
540	2.60
630	2.90
750	3.25
4 days	4.39

[a]0.012M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-13a

Rate Constant Derived from Table A-13[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	2.76 ± 0.03	0.997

[a]Error for individual run is the standard deviation from a least square analysis.

Figure A-13

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-13

(a-x) = (titer at infinite time - titer at time, t)

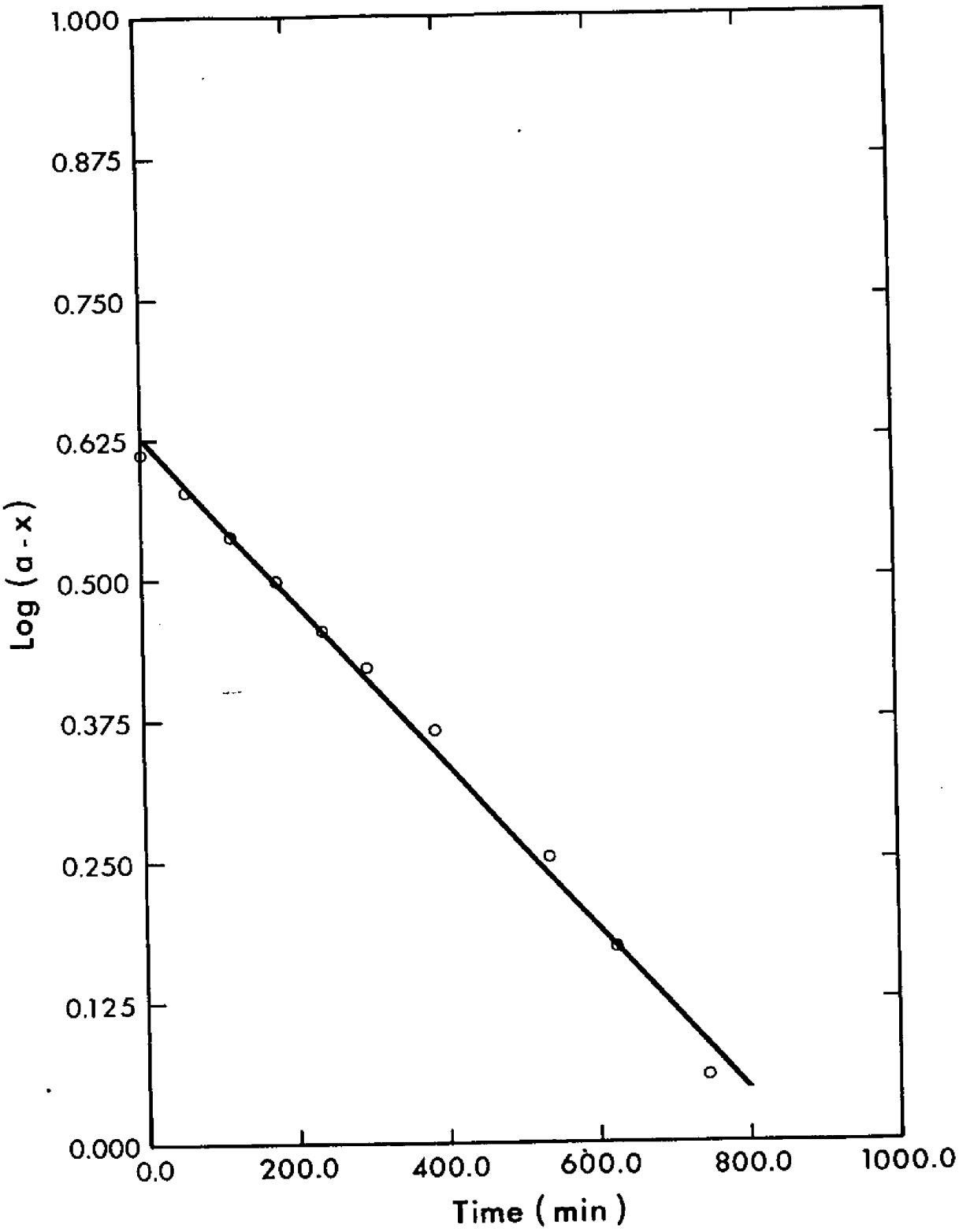

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
200.0
400.0
600.0
800.0
1000.0
Time (min)

Table A-14

Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 80 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time, hours	ml titrant[a] required for 5 ml aliquot
	run 1
	(ca. 0.013M I)[b]
0	0.50
2	0.70
5	1.36
8	1.95
13.5	2.83
23.5	3.85
27.5	4.14
31.25	4.40
6 days	5.93

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-14a

Rate Constant Derived from Table A-14[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	1.15 ± 0.01	0.999

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-14

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-14

(a-x) = (titer at infinite time - titer at time, t)

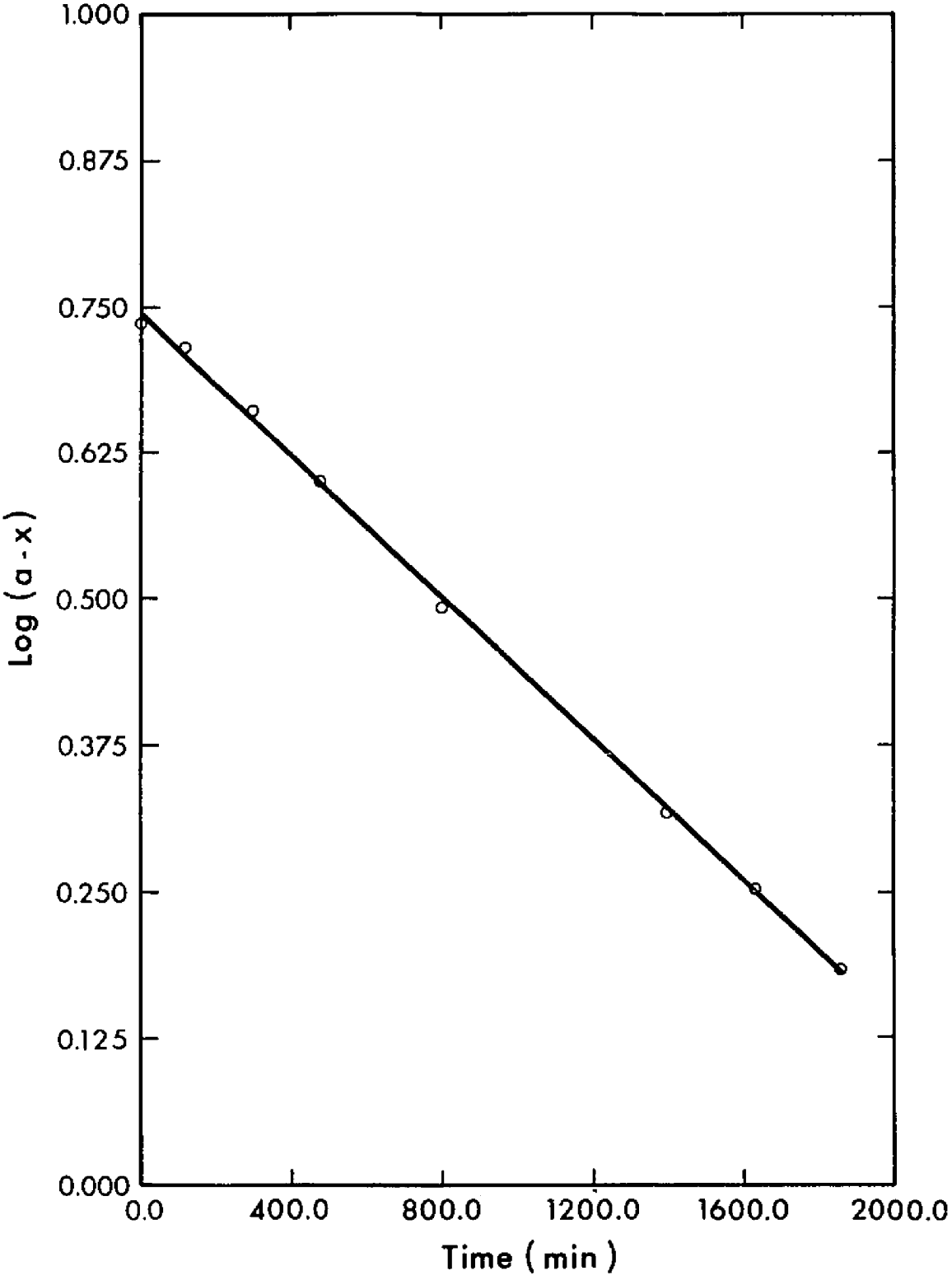

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
400.0
800.0
1200.0
1600.0
2000.0
Time (min)

Table A-15

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 65 Volume % Aqueous Methanol at 80.0° ± 0.10°

time,min	ml titrant[a] required for 5 ml aliquots	
	run 1 (ca. 0.019M I)[b]	run 2 (ca. 0.019M I)
0	0.55	0.45
30	2.05	2.23
60	3.40	3.40
90	4.35	4.33
120	5.15	5.15
150	5.80	5.75
180	6.07	6.13
210	6.60	6.55
255	7.05	6.95
2 days	7.95	7.95

[a]0.012M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-15a

Rate Constants Derived from Table A-15[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	13.3 ± 0.1	0.998
2	13.1 ± 0.1	0.999

[a]Error for individual run is the standard deviation from a least square analysis.

Figure A-15

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-15

(a-x) = (titer at infinite time - titer at time, t)

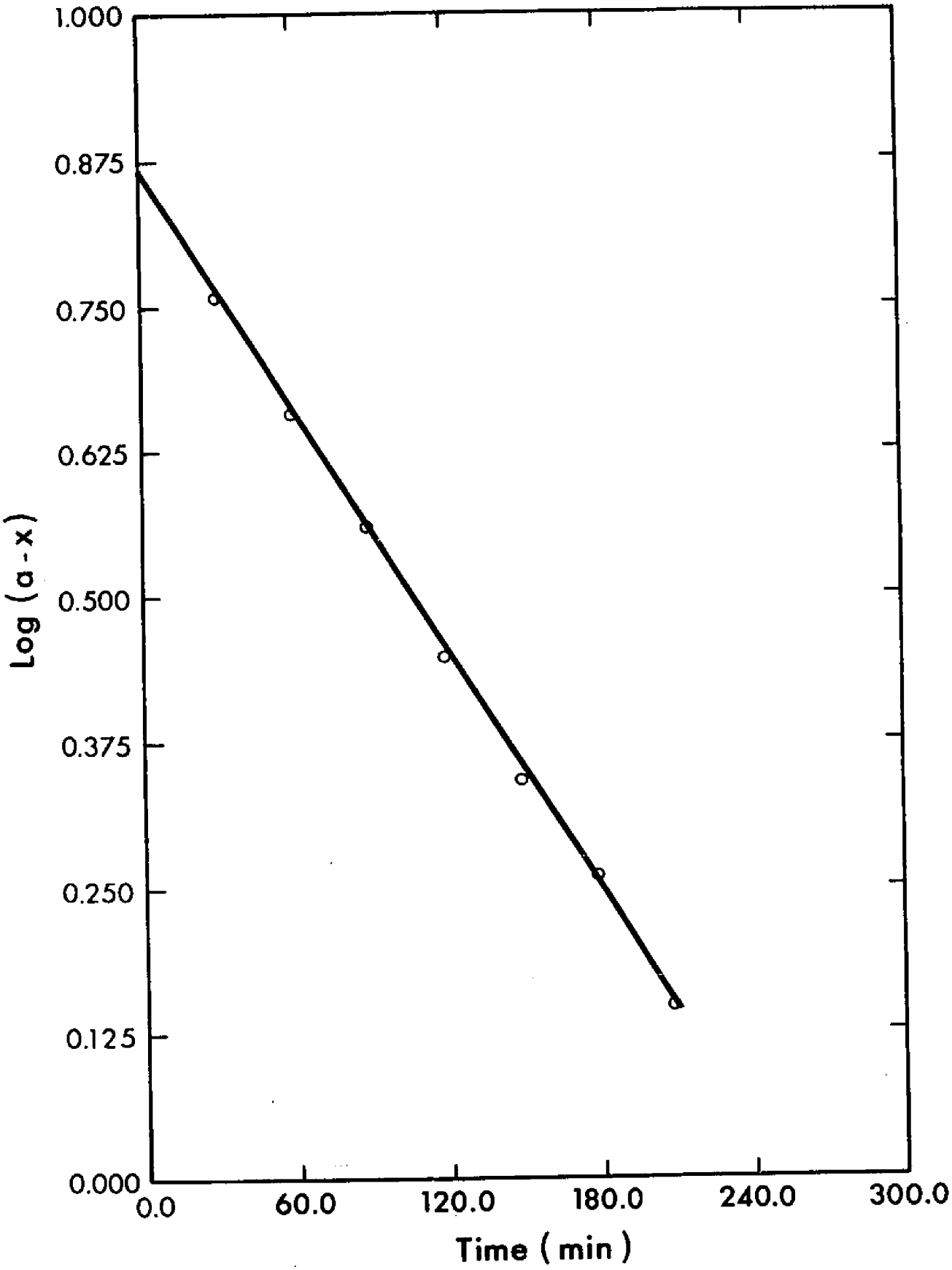

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
60.0
120.0
180.0
240.0
300.0
Time (min)

Table A-16

The Solvolysis of 2-Bromo-2-trimethylsilylpropane(I)

in 65 Volume % Aqueous Acetone at 80.0° ± 0.1

time, min	ml titrant[a] required for 5 ml aliquot	
	run 1 (ca. 0.014M I)[b]	run 2 (ca. 0.014M I)
0	0.36	0.40
30	0.56	0.50
60	0.76	0.76
105	1.12	1.05
150	1.25	1.20
195	1.45	1.45
255	1.72	1.85
315	2.25	2.25
450	2.45	2.55
495	2.85	2.82
540	3.01	3.01
3 days	6.00	6.00

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-16a

Rate Constants Derived from Table A-16[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	1.90 ± 0.03	0.993
2	1.93 ± 0.02	0.996

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-16

Solvolysis of 2-Bromo-2-trimethylsilylpropane

Data taken from Table A-16, run 2

(a-x) = (titer at infinite time - titer at time, t)

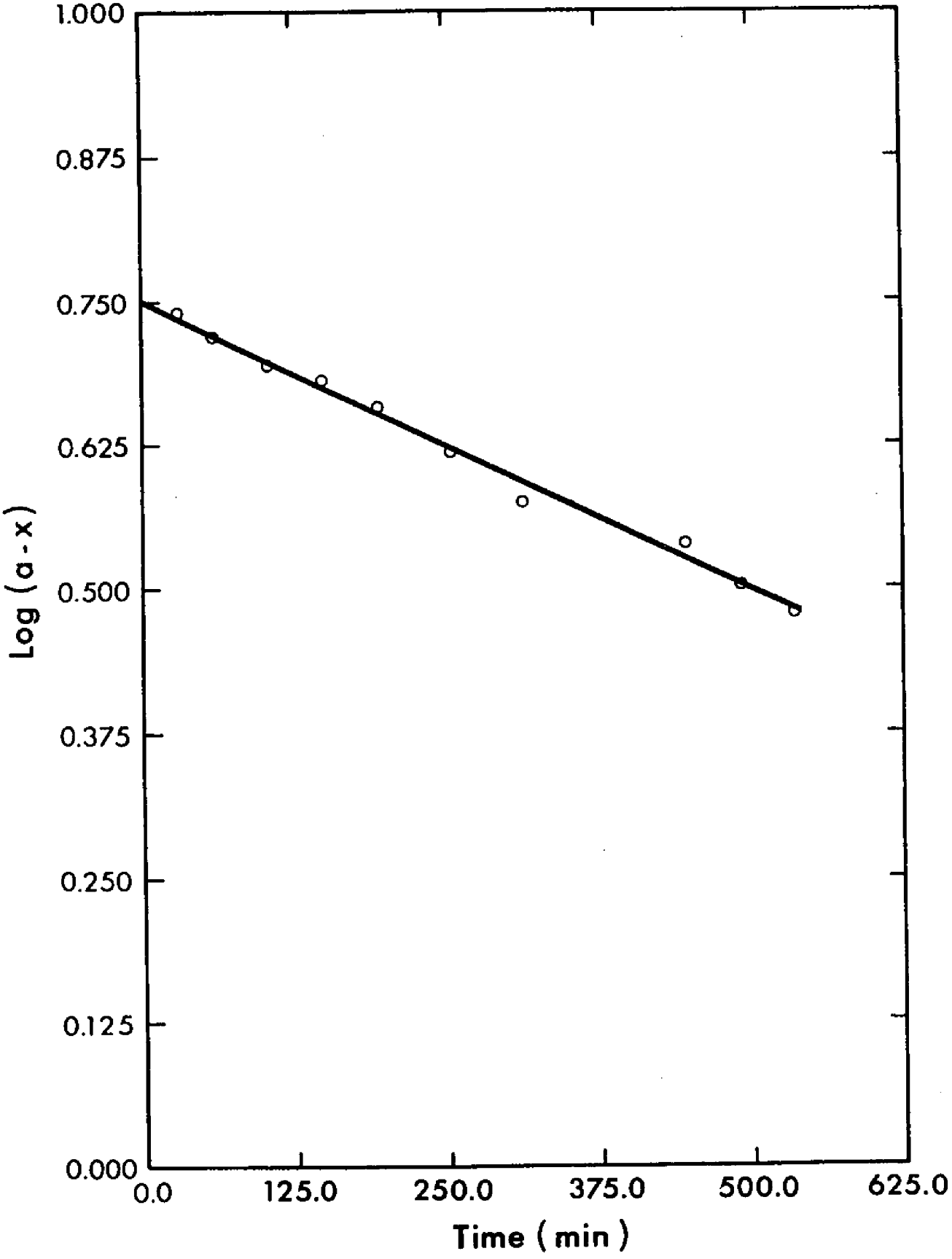

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
125.0
250.0
375.0
500.0
625.0
Time (min)

Table A-17

The Solvolysis of 2-Bromo-2-(phenyldimethylsilyl)propane(I)

in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquot			
	run 1 (.015M I)[b]	run 2 (.015M I)	run 3 (.013M I)	run 4 (.013M I)
0	0.45	0.40	0.56	0.55
45			1.30	1.30
60	1.35	1.28		
90	1.95	1.83	1.90	1.86
135			2.45	2.50
145	2.60	2.65		
180	3.10	2.98	2.91	2.85
240			3.43	3.50
250	3.64	3.60		
285			3.85	3.80
305	4.06	4.06		
330			4.15	4.10
365	4.51	4.55		
375			4.40	4.38
420	4.85	4.90	4.67	4.70
470	5.10	5.10		
72 hours	6.59	6.59	6.10	6.10

[a] 0.015M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-17a

Rate Constants Derived from Table A-17[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	5.01 ± 0.02	0.999
2	5.13 ± 0.03	0.999
3	5.27 ± 0.02	0.999
4	5.27 ± 0.03	0.999

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-17

Solvolysis of 2-Bromo-2-(phenyldimethylsilyl)propane

Data taken from Table A-17, run 1

(a-x) = (titer at infinite time - titer at time, t)

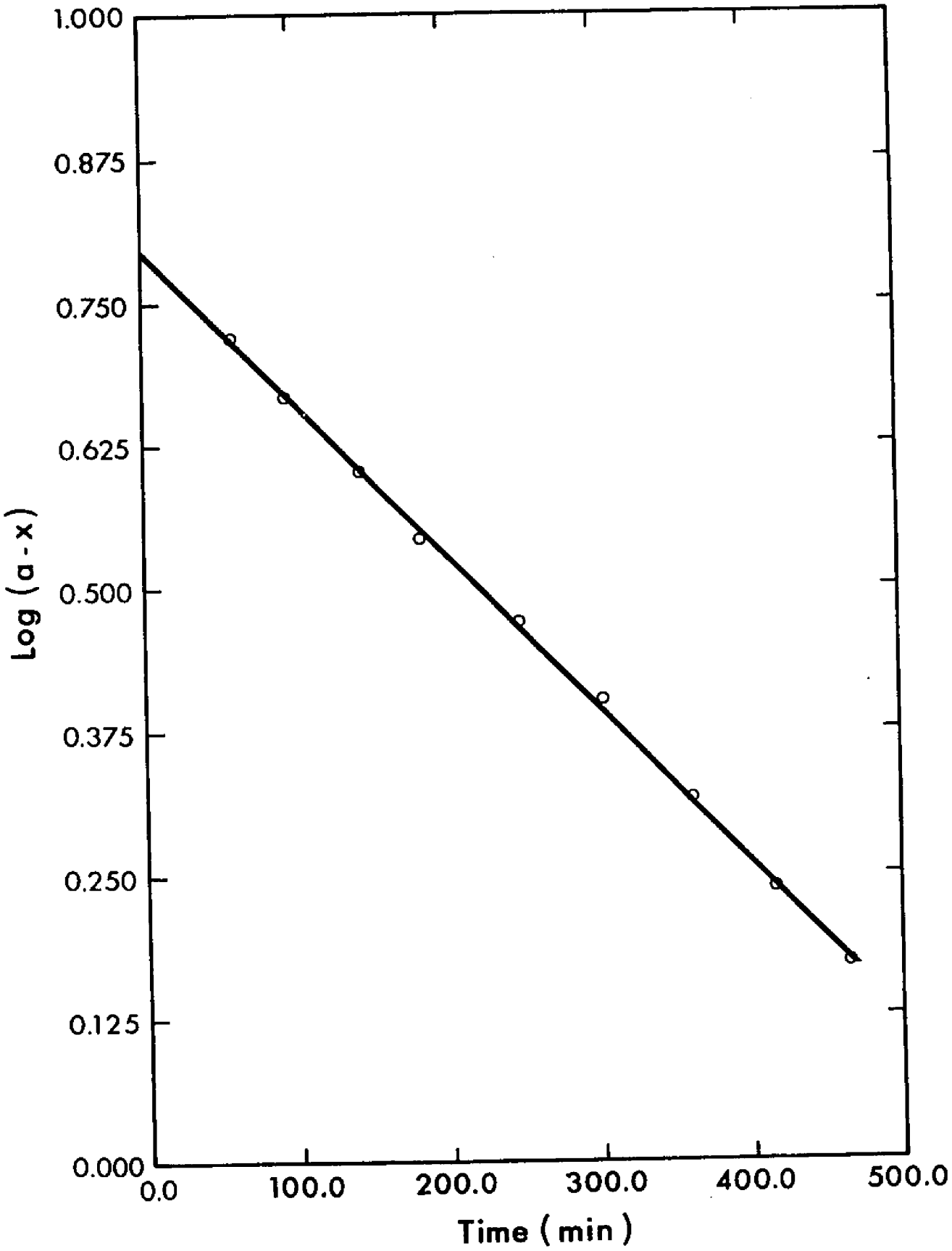

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
100.0
200.0
300.0
400.0
500.0
Time (min)

Table A-18

The Solvolysis of 2-Bromo-2-(p-tolyldimethylsilyl)propane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots			
	run 1 (.013M I)[b]	run 2 (.013M I)	run 3 (.014M I)	run 4 (.014M I)
0	0.74	0.73	0.35	0.35
45	1.34	1.36		
60			1.95	1.55
90			2.20	2.30
100	2.20	2.22		
120			2.78	2.82
150	2.98	2.90	3.18	3.23
180			3.78	3.72
220	3.65	3.70		
240			4.40	4.35
280	4.05	4.10		
300			4.90	4.86
375	4.66	4.60	5.37	5.35
420			5.55	5.52
440	5.06	4.96		
4 days	5.60	5.60	6.37	6.37

[a]0.013M NaOH; cresol red, indicator.

[b]See experimental section concerning preparation of solution.

Table A-18a

Rate Constants Derived from Table A-18[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	7.28 ± 0.09	0.997
2	7.23 ± 0.05	0.999
3	8.09 ± 0.06	0.998
4	7.79 ± 0.06	0.998

[a]Error for individual run is the standard deviation from a least square analysis.

Figure A-18

Solvolysis of 2-Bromo-2-(p-tolyldimethylsilyl)propane

Data taken from Table A-18, run 2

(a-x) = (titer at infinite time - titer at time, t)

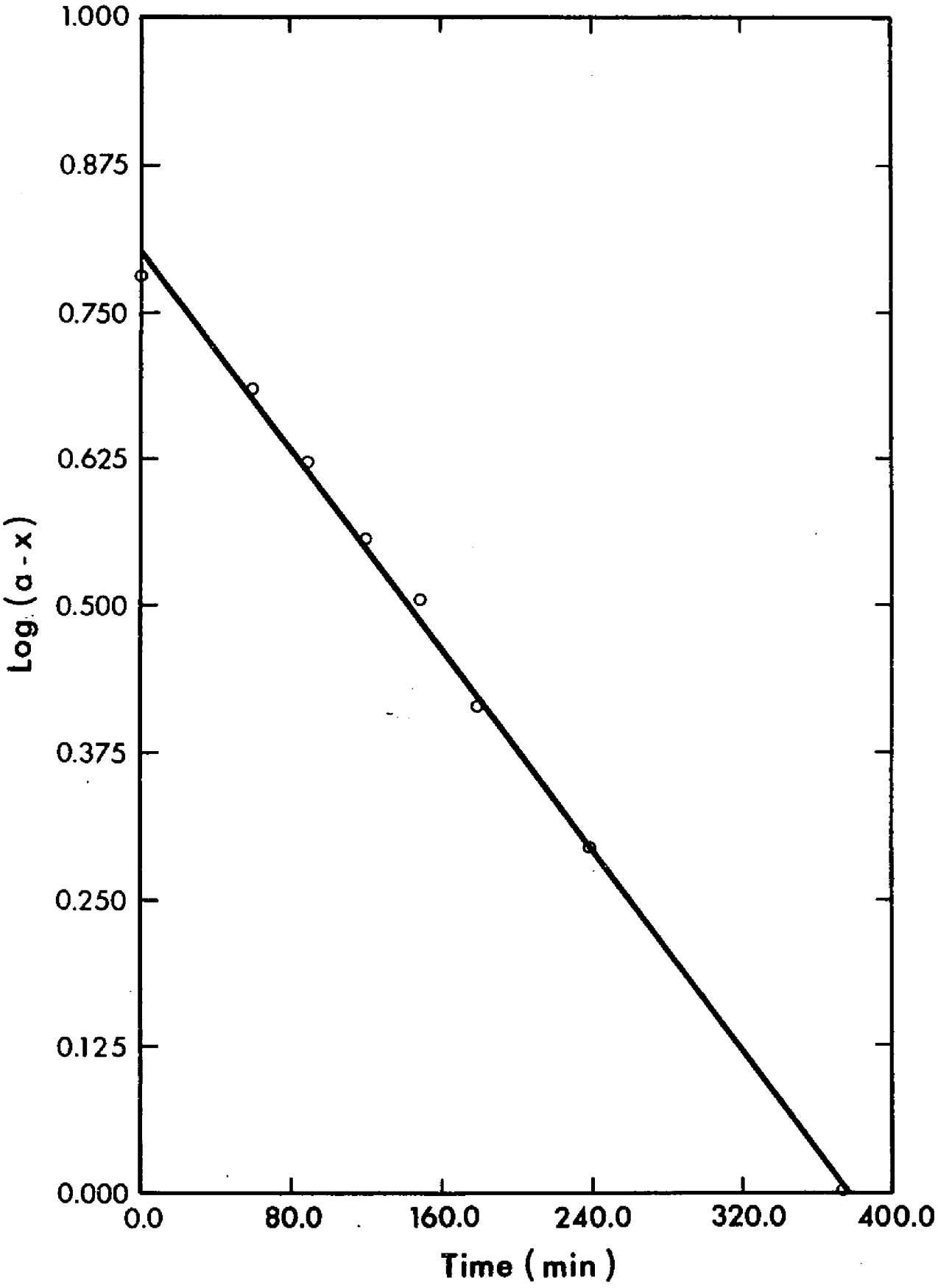

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
80.0
160.0
240.0
320.0
400.0
Time (min)

Table A-19

The Solvolysis of 2-Bromo-2-(p-chlorophenyldimethylsilyl)propane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml of titrant[a] required for 5 ml aliquots		
	run 1[b] (.0137M I)[c]	run 2 (.0135M I)	run 3 (.0135M I)
0	0.72	0.37	0.36
50		0.77	0.75
90	1.70	1.00	1.05
120		1.26	1.40
180	3.15	1.61	1.65
240		2.03	2.11
270	4.08		
330		2.55	2.49
360	5.01		
455	5.73	3.05	3.03
525		3.27	3.27
540	6.45		
3 days	9.90	5.10	5.10

[a]0.012M NaOH; cresol red, indicator.

[b]10 ml aliquots used.

[c]See experimental section concerning preparation of solution.

Table A-19a

Rate Constants Derived from Table A-19[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	3.05 ± 0.03	0.998
2	3.06 ± 0.02	0.999
3	3.01 ± 0.02	0.999

[a]Error for individual run is the standard deviation from a least square analysis.

Figure A-19

Solvolysis of 2-Bromo-2-(p-chlorophenyldimethylsilyl)propane

Data taken from Table A-19, run 2

(a-x) = (titer at infinite time - titer at time, t)

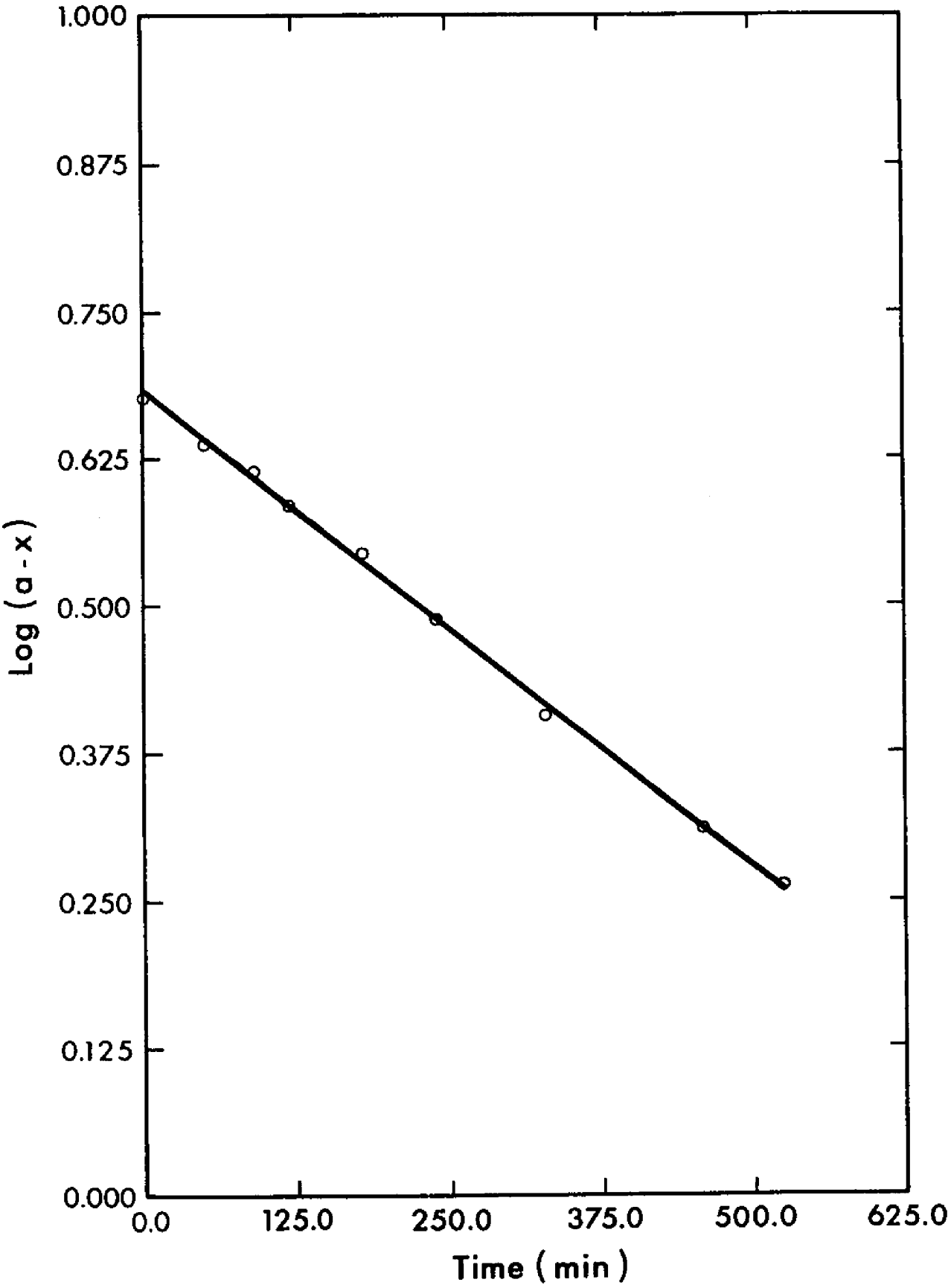

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
125.0
250.0
375.0
500.0
625.0
Time (min)

Table A-20

The Solvolysis of 2-Bromo-2-(p-anisyldimethylsilyl)propane(I)

in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots		
	run 1 (.012M I)[c]	run 2 (.011M I)	run 3 (.011M I)
0	0.80	0.40	0.50
30	2.15	0.90	0.90
50		1.26	1.40
60	3.75		
70		1.95	1.80
90	4.85	2.03	2.02
120	5.75	2.18	2.26
150	6.58	2.65	2.60
180	7.30	2.96	2.96
210	7.94	3.19	3.20
240		3.40	3.37
3 days	10.93	4.43	4.43

[a] 0.012M NaOH; cresol red, indicator.

[b] 10 ml aliquots.

[c] See experimental section concerning the preparation of solution.

Table A-20a

Rate Constants Derived from Table A-20[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	10.01 ± 0.07	0.999
2	9.50 ± 0.10	0.997
3	9.20 ± 0.09	0.997

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-20

Solvolysis of 2-Bromo-2-(p-anisyldimethylsilyl)propane

Data taken from Table A-20, run 2

(a-x) = (titer at infinite time - titer at time, t)

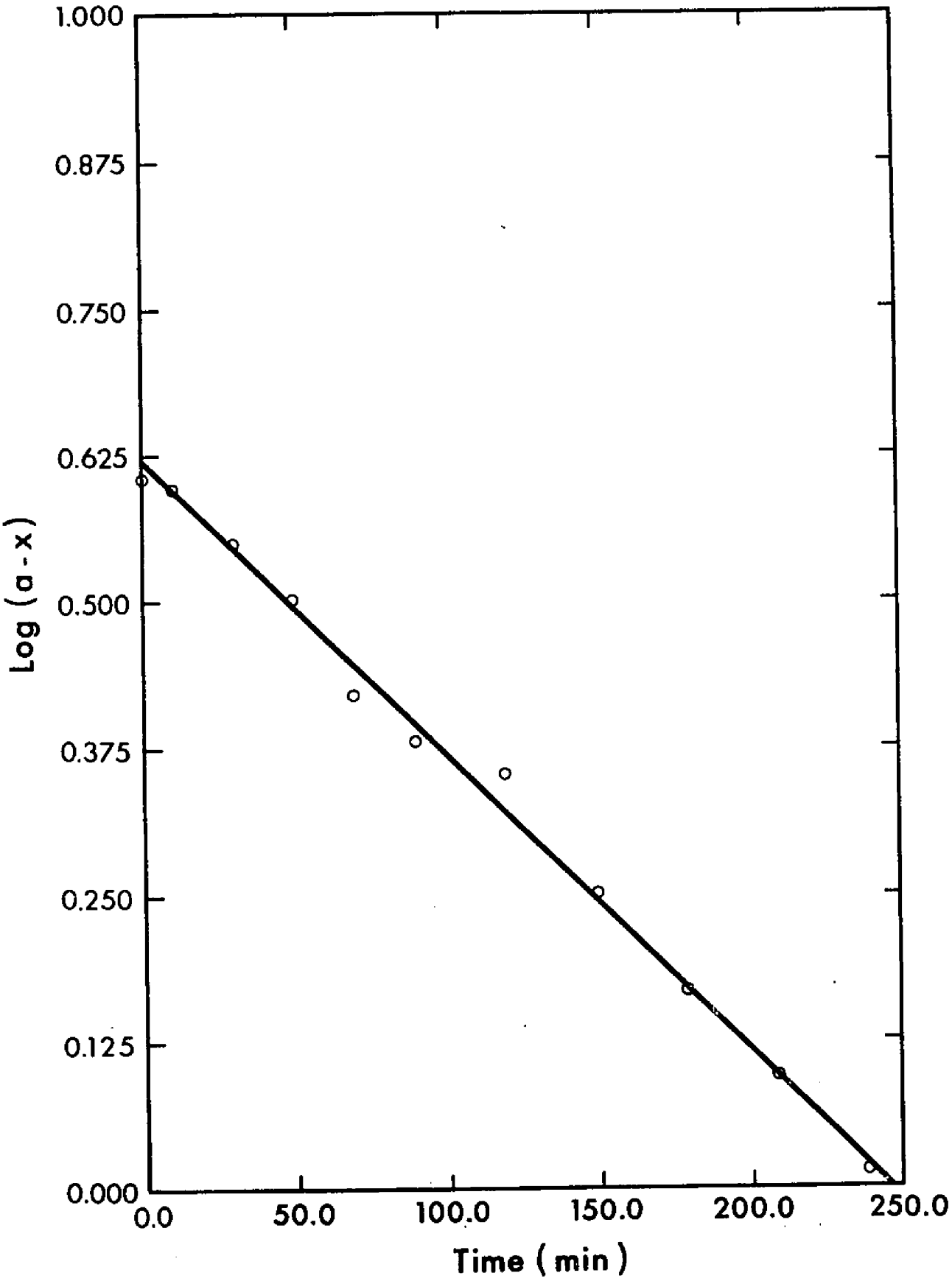

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
50.0
100.0
150.0
200.0
250.0
Time (min)

Table A-21

The Solvolysis of 2-Bromo-2-(p-fluorodimethylsilyl)propane in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots		
	run 1[b] (.0092M I)	run 2 (.0128M I)	run 3 (.0128M I)
0	0.65	0.63	0.70
60	1.45	1.18	1.10
105		1.55	1.65
120	2.45		
165		2.20	2.20
180	3.10		
210		2.65	2.70
255		3.00	2.97
270	3.95		
300		3.26	3.25
345		3.57	3.58
390	5.20	3.89	3.94
475	5.70		
4 days	8.33	6.20	6.20

[a] 0.012M NaOH; cresol red, indicator.

[b] 10 ml aliquots

[c] See experimental section concerning preparation of solution.

Table A-21a

Rate Constants Derived from Table A-21[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	3.84 ± 0.04	0.998
2	3.80 ± 0.03	0.998
3	3.96 ± 0.03	0.998

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-21

Solvolysis of 2-Bromo-2-(p-fluorophenyldimethylsilyl)propane

Data taken from Table A-21, run 2

(a-x) = (titer at infinite time - titer at time, t)

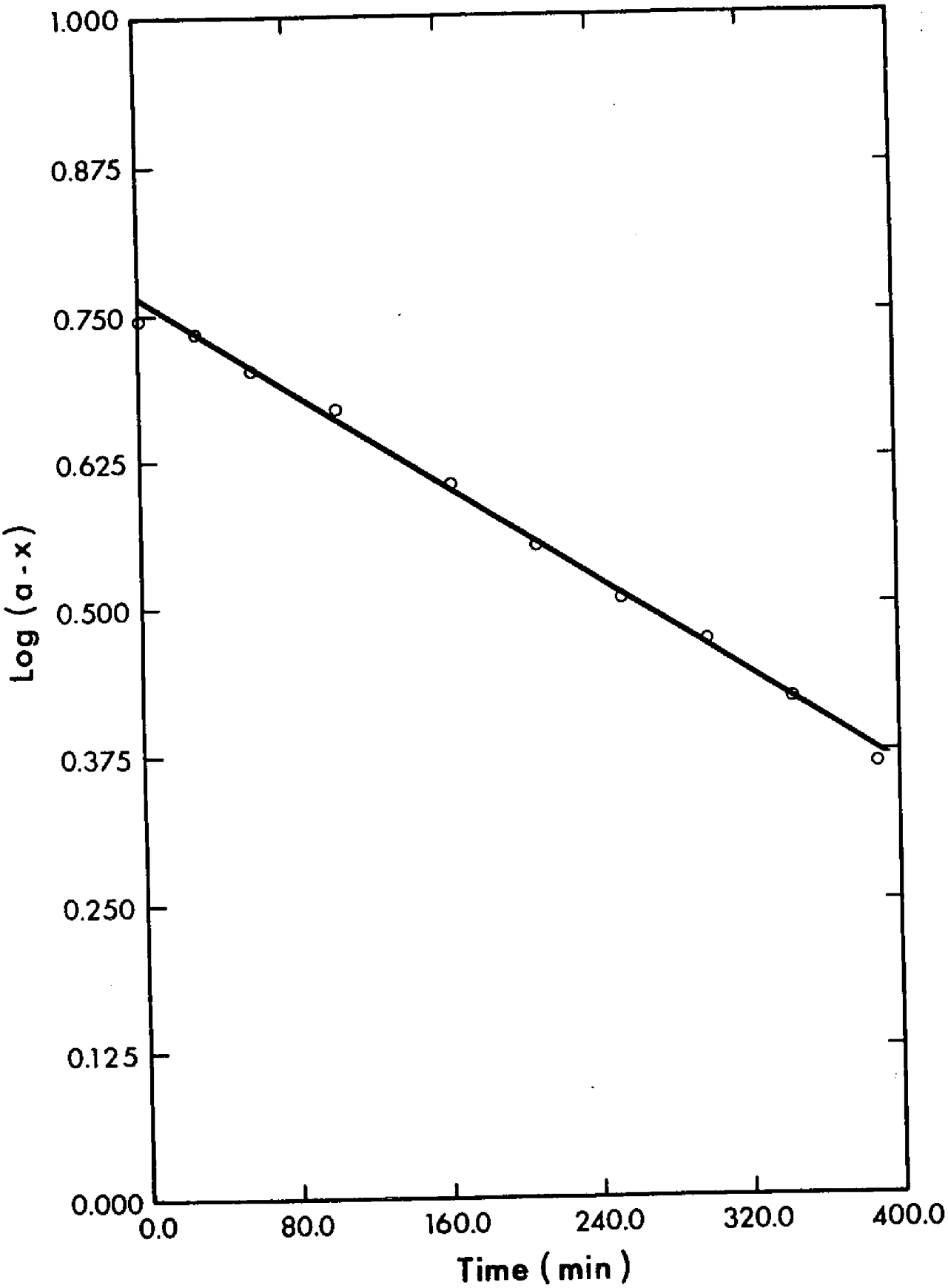

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
80.0
160.0
240.0
320.0
400.0
Time (min)

Table A-22

The Solvolysis of 2-Bromo-2-(m-tolyldimethylsilyl)propane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 5 ml aliquots		
	run 1[b] (.0125M I)	run 2 (.013M I)	run 3 (.013M I)
0	0.92	0.47	0.48
45		1.10	1.10
60	2.90		
90		1.77	1.82
120	4.51		
135		2.34	2.34
180		2.90	2.95
190	6.00		
225		3.30	3.30
260	7.10		
285		3.82	3.75
330	7.86	3.95	4.00
390	8.40	4.35	4.30
3 days	10.50	5.65	5.65

[a]0.012M NaOH, cresol red, indicator.

[b]10 ml aliquots.

[c]See experimental section concerning preparation of solution.

Table A-22a

Rate Constants Derived from Table A-22[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	6.49 ± 0.03	0.999
2	5.86 ± 0.05	0.998
3	5.84 ± 0.03	0.999

[a]Error for individual run is the standard deviation from least square analysis.

Figure A-22

Solvolysis of 2-Bromo-2-(m-tolyldimethylsilyl)propane

Data taken from Table A-22, run 2

(a-x) = (titer at infinite time - titer at time, t)

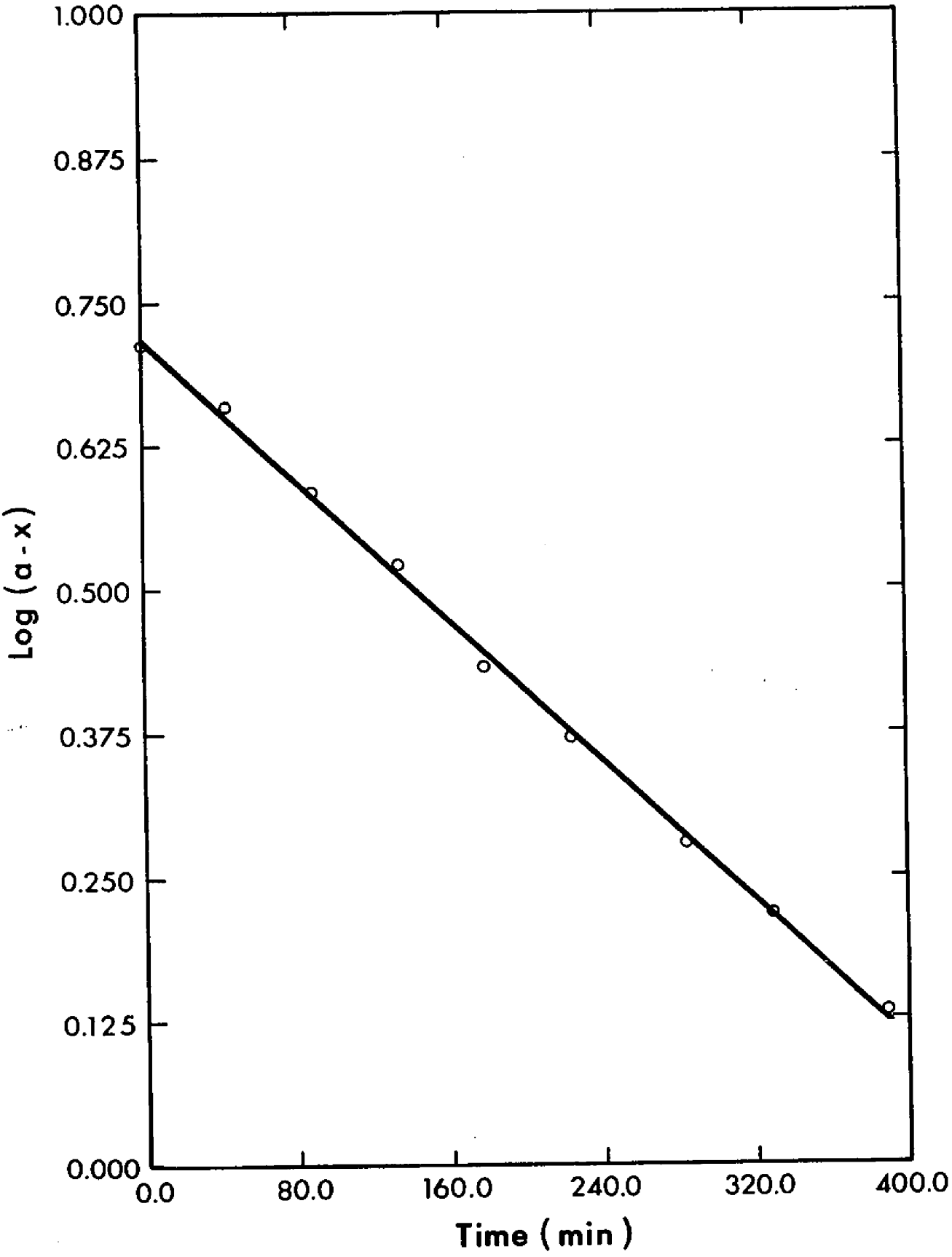

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
80.0
160.0
240.0
320.0
400.0
Time (min)

Table A-23

The Solvolysis of 2-Bromo-2-(m-chlorophenyldimethylsilyl)propane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml of titrant[a] required for 5 ml aliquots		
	run 1[b] (ca. 0.01M I)[c]	run 2 (ca. 0.011M I)	run 3 (ca. 0.011M I)
0	0.50	0.42	0.38
90	1.55		
105		0.91	0.87
165		1.10	1.10
180	2.05		
260		1.53	1.51
300	3.06		
330		1.72	1.80
365	3.38		
405		2.00	2.02
480	4.00	2.20	2.16
550	4.60		
590		2.50	2.53
695	3.50		
855		2.90	2.85
4 days	8.70	4.70	4.70

[a] 0.012M NaOH; cresol red, indicator.

[b] 10 ml aliquots.

[c] See experimental section concerning preparation of solution.

Table A-23a

Rate Constants Derived from Table A-23[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	2.01 ± 0.02	0.997
2	1.75 ± 0.02	0.996
3	1.74 ± 0.06	0.975

[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-23

Solvolysis of 2-Bromo-2-(m-chlorophenyldimethylsilyl)propane

Data taken from Table A-23, run 2

(a-x) = (titer at infinite time - titer at time, t)

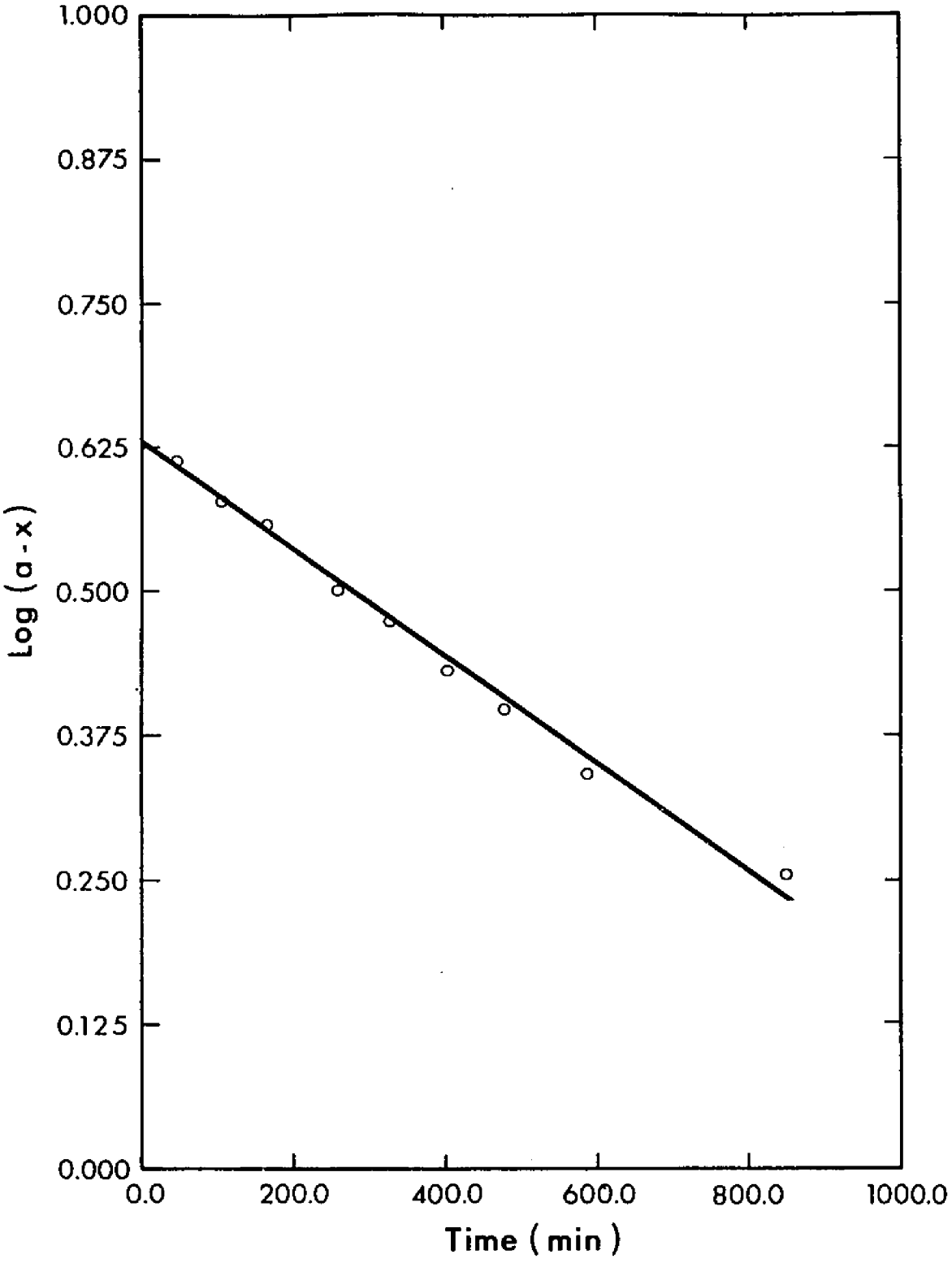

1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
200.0
400.0
600.0
800.0
1000.0
Time (min)

Table A-24

The Solvolysis of 2-Bromo-2-(p-bromophenyldimethylsilyl)propane(I) in 54 Volume % Aqueous Ethanol at 80.0° ± 0.1°

time,min	ml titrant[a] required for 10 ml aliquots		
	run 1 (ca. 0.009M I)[b]	run 2 (ca. 0.01M I)	run 3 (ca. 0.01M I)
0	0.55	0.44	0.33
60		0.95	0.95
90	1.40		
120		1.63	1.63
180	1.92	2.10	2.20
255		2.77	2.79
270	2.35		
315		3.32	3.35
360	2.65		
390		3.86	3.83
450	3.10		
480		4.36	4.30
540	3.50		
615		5.01	5.01
4 days	5.60	7.50	7.50

[a] 0.012M NaOH; cresol red, indicator.

[b] See experimental section concerning preparation of solution.

Table A-24a

Rate Constants Derived from Table A-24[a]

Run	k x 10^5, sec^{-1}	Correlation Coefficient
1	2.57 ± 0.10	0.996
2	2.85 ± 0.02	0.999
3	2.87 ± 0.01	0.999

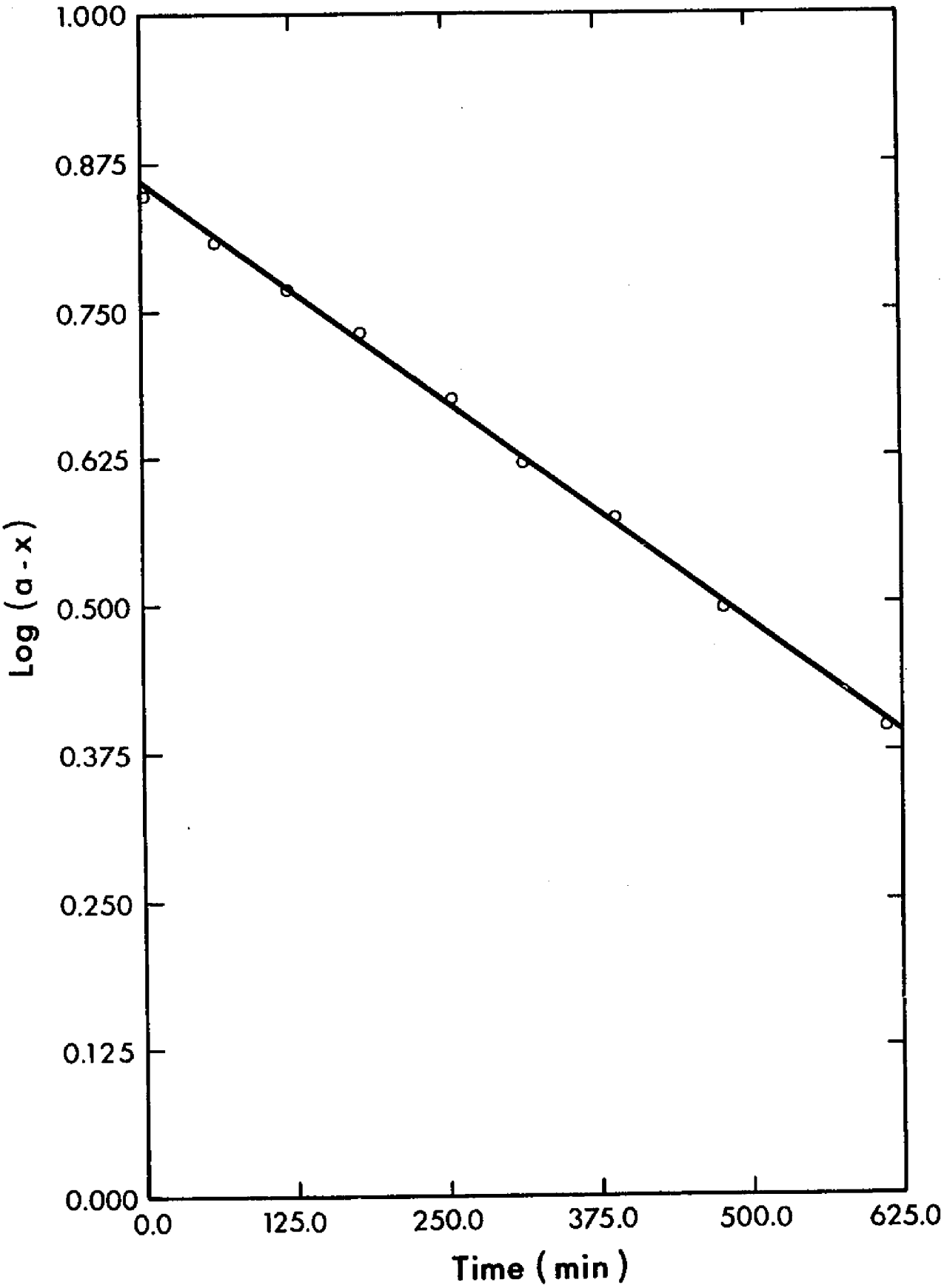
[a] Error for individual run is the standard deviation from a least square analysis.

Figure A-24

Solvolysis of 2-Bromo-2-(p-bromophenyldimethylsilyl)propane

Data taken from Table A-24, run 2

(a-x) = (titer at infinite time - titer at time, t)


1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
Log (a - x)
0.0
125.0
250.0
375.0
500.0
625.0
Time (min)

VITA

John Paul Jones was born on February 5, 1943 in Houston, Texas, where he was educated in both public and private school systems. In June, 1961, he graduated from Harding Academy High School, Searcy, Arkansas.

He entered Robert E. Lee Junior College of Baytown, Texas in the summer of 1961 and transferred to Harding College in September, 1961 where he received the degree of Bachelor of Science in chemistry in June, 1965.

The following September, he entered the Graduate School of Louisiana State University in Baton Rouge, where he is now a candidate for the degree of Doctor of Philosophy in chemistry.

On December 22, 1966, he married Linda Lee Stafford of Neosho, Missouri. He is the father of two children, Tracy Alan and Johnna Lin.

Honorary and Professional Societies

Phi Lambda Upsilon

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Positions

Laboratory Assistant, Harding College, 1965.

Research Assistant, Louisiana State University 1967-69, 1971.

Esso Education Foundation Research Participant, Louisiana State University, 1970.

Director of Organic Laboratories, Mississippi State University, State College, Mississippi, 1971-72.

EXAMINATION AND THESIS REPORT

Candidate: John Paul Jones

Major Field: Chemistry

Title of Thesis: Reactions of α-Halosilanes

Approved:

F K Cartledge
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

H Kwart

Paul Kinney

Joel Selbin

H B Williams

Date of Examination:

July 9, 1971